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PREFACE

This report summarizes the in-house and subcontracted research and development (R&D) activities under the National Renewable Energy Laboratory (NREL) Photovoltaic (PV) Program from October 1, 1992, through September 30, 1993 (fiscal year [FY] 1993). The NREL PV Program is part of the U.S. Department of Energy's (DOE's) National Photovoltaics Program, as described in the DOE Photovoltaics Program Plan, FY 1991 - FY 1995. The mission of the DOE National Photovoltaics Program is to develop PV technology for large-scale generation of economically competitive electric power in the United States. The major challenge in fulfilling the mission is to assist the U.S. PV industry and user communities in laying the foundation for installing at least 1000 MW of electrical capacity generated by PV by the year 2000.

The FY 1993 budget authority (BA) for carrying out the NREL PV Program was $40.1 million in operating funds and $0.9 million in capital equipment funds. An additional $4.8 million in capital equipment funds were made available for the new Solar Energy Research Facility (SERF) that will house the in-house PV laboratories beginning in FY 1994. Subcontract activities represent a major part of the NREL PV Program, with more than $23.7 million (nearly 59%) of the FY 1993 operating funds going to 70 subcontractors. In FY 1993, DOE assigned certain other PV subcontracting efforts to the DOE Golden Field Office (DOE/GO), and assigned responsibility for their technical support to the NREL PV Program. An example is the PV:BONUS (Building Opportunities in the U.S. for Photovoltaics) Project.

The NREL PV Program activities involve conducting basic, applied, and engineering research; managing subcontracted R&D projects; performing research complementary to subcontracted work; developing and maintaining state-of-the-art measurement and device capabilities; supporting PV manufacturing technology and module development; transferring results to industry; and evolving viable partnerships for PV systems and market development. The program is carried out under six project areas: Crystalline Materials and Advanced Concepts, Polycrystalline Thin Films, Amorphous Silicon, Photovoltaic Manufacturing Technology, PV Module and System Performance and Engineering, and PV Analysis and Applications Development.

Approved for the NATIONAL RENEWABLE ENERGY LABORATORY

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Basic Sciences Division

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EXECUTIVE SUMMARY

This report summarizes the in-house and subcontracted research and development (R&D) activities under the National Renewable Energy Laboratory (NREL) Photovoltaic (PV) Program from October 1, 1992, through September 30, 1993 (fiscal year [FY] 1993). The NREL PV Program is part of the U.S. Department of Energy's (DOE's) National Photovoltaics Program, as described in the DOE Photovoltaics Program Plan, FY 1991 - FY 1995. The mission of the DOE National Photovoltaics Program is to develop PV technology for large-scale generation of economically competitive electric power in the United States. The major challenge in fulfilling the mission is to assist the U.S. PV industry and user communities in laying the foundation for installing at least 1000 MW of electrical capacity generated by PV by the year 2000.

The FY 1993 budget authority (BA) for carrying out the NREL PV Program was $40.1 million in operating funds and $0.9 million in capital equipment funds. An additional $4.8 million in capital equipment funds were made available for the new Solar Energy Research Facility (SERF) that will house the in-house PV laboratories beginning in FY 1994. Subcontract activities represent a major part of the NREL PV Program, with more than $23.7 million (nearly 59%) of the FY 1993 operating funds going to 70 subcontractors. In FY 1993, DOE assigned certain other PV subcontracting efforts to the DOE Golden Field Office (DOE/GO), and assigned responsibility for their technical support to the NREL PV Program. An example is the PV:BONUS (Building Opportunities in the U.S. for Photovoltaics) Project.

Major program thrusts in FY 1993 continued to be implemented based on DOE's Photovoltaics Program Plan FY 1991-FY 1995. In FY 1993, the balance of activities was readjusted according to changing DOE PV Program priorities. The DOE goal over the next few years will be to lay the groundwork for a growing U.S. PV technology and industrial base with increased emphasis on market and project development activities with industry. To accomplish this, the program's policy now embraces three relatively equal priority activities: 1) technology development and validation, 2) market conditioning, and 3) project venturing.

NREL's PV activities include conducting research at the laboratory as well as managing subcontracted R&D projects. The primary research activities are conducted in advanced PV material technologies, including amorphous silicon thin-film materials; polycrystalline thin films, such as copper indium diselenide, cadmium telluride, and their alloys; and high-efficiency crystalline cells, including silicon and gallium arsenide and their alloys. Improving the way that PV devices are manufactured is vital. Two complementary approaches are pursued. One involves government/industry partnerships under the PV Manufacturing Technology (PVMaT) Project. That approach focuses on improving manufacturing processes and products, accelerating manufacturing cost reduction, and laying the foundation for increased production capacity. The second approach involves module development research to evaluate modules and module performance and suggest solutions to manufacturers' module problems. System engineering and market and applications development round out the balanced approach pursued. NREL subcontracts also support the continued influx of new ideas and highly qualified university research teams to expand the current limits of PV technology. Transferring research results into commercial products and applications in a timely and effective manner is another major activity of NREL's PV Program.
The research activities under the program are summarized under six project areas: Crystalline Materials and Advanced Concepts Project, Polycrystalline Thin Films Project, Amorphous Silicon Research Project, Photovoltaic Manufacturing Technology (PVMaT) Project, PV Module and System Performance and Engineering Project, and PV Analysis and Applications Development Project. Each project area includes a brief overview of the objectives, approaches, and some key developments. Following that are technical summaries of the in-house and subcontract activities. Finally, lists of FY 1993 subcontracts and major research publications and subcontractor reports are presented.
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1.0 INTRODUCTION

This report reviews the in-house and subcontracted research and development (R&D) activities under the National Renewable Energy Laboratory (NREL) Photovoltaic (PV) Program from October 1, 1992, through September 30, 1993 (fiscal year [FY] 1993). The NREL PV Program is part of the U.S. Department of Energy's (DOE's) National Photovoltaics Program, as described in the DOE Photovoltaics Program Plan, FY 1991 - FY 1995. The FY 1993 budget authority (BA) for carrying out the NREL PV Program was $40.1 million in operating funds and $0.9 million in capital equipment funds. An additional $4.8 million in capital equipment funds were made available for the new Solar Energy Research Facility (SERF) that will house the in-house PV laboratories beginning in FY 1994. Subcontract activities represent a major part of the NREL PV Program, with more than $23.7 million (nearly 59%) of the FY 1993 operating funds going to 70 subcontractors. In FY 1993, DOE assigned certain other PV subcontracting efforts to the DOE Golden Field Office (DOE/GO), and assigned responsibility for their technical support to the NREL PV Program. An example is the PV:BONUS (Building Opportunities in the U.S. for Photovoltaics) Project. These DOE/GO efforts are also reported in this document.

1.1 Background

The NREL PV Program is part of the DOE National Photovoltaics Program managed by the Photovoltaics Technology Division in the Office of Solar Energy Conversion (OSEC). OSEC is under the Office of Utility Technologies in DOE's Office of Energy Efficiency and Renewable Energy.

Major program thrusts in FY 1993 continued to be implemented based on DOE's Photovoltaics Program Plan FY 1991-FY 1995. The mission of the national PV Program is to develop PV technology for large-scale generation of economically competitive electric power in the United States. The major challenge in fulfilling the mission is to assist industry in laying the foundation for the installation of at least 1000 MW of electrical capacity generated by PV by the year 2000. In FY 1993, the balance of activities was readjusted according to changing DOE PV Program priorities. The DOE goal over the next few years will be to lay the groundwork for a growing U.S. PV technology and industrial base with increased emphasis on market and project development activities with industry. To accomplish this, the program's policy now embraces three relatively equal priority activities: 1) technology development and validation, 2) market conditioning, and 3) project venturing. The new policy will continue a strong technology development program but will emphasize R&D for the technologies and companies that are positioned to achieve substantial market penetration, price reductions, and manufacturing scaleup. Program activities include continuing efforts at forming partnerships with manufacturers and utilities (the ultimate benefactors and users), with universities, and with federal and state agencies.

Under the DOE PV Program, the NREL PV Program supports fundamental and applied R&D, manufacturing development, and systems and market development in PV energy technology. The project also provides services to industry and electric utilities or other users, and it provides overall programmatic support for the national PV program. The NREL subcontract program is responsible for most of the R&D, manufacturing technology development, and some of the
systems and market development task areas under the national PV program. The implementation of the subcontract program is based on competitive public solicitations. One of the most important subcontracting mechanisms is in the form of government/industry partnerships, with industry sharing the cost of research with DOE/NREL. Increasing emphasis is being directed to more closely working with industry, utilities, and other end users on PV manufacturing technology, systems, and market needs. Approaches for this increasing emphasis include mitigating barriers to PV adoption in the utility and international marketplace and project venturing with decision makers/organizations representing target market sectors for PV (i.e., utilities, buildings, transportation, and industry). As appropriate for the system and market development areas, NREL is supporting activities such as education; technical assistance and training; market, economic, and financial analysis; technology characterizations; regulatory, rate, and value analysis; codes and standards assessment and development; participation involving working with customers in project development activities; and cofinancing of projects to lower costs to a level competitive with more conventional energy options. The project venturing, or "stakeholder" approach should lead to significant cost reductions while developing a strong market base for suppliers. Under project venturing, DOE is placing particular emphasis on supporting and strengthening programs that are already in place, such as PV:BONUS, the Americas’ 21st Century Project, and the recently formed Utility Photovoltaics Group (UPVG).

NREL’s PV activities include conducting research at the laboratory as well as managing subcontracted R&D projects. The primary research activities are conducted in advanced PV material technologies, including amorphous silicon thin-film materials; polycrystalline thin films, such as copper indium diselenide, cadmium telluride, and their alloys; and high-efficiency crystalline cells, including silicon and gallium arsenide and their alloys. Improving the way that PV devices are manufactured is vital. Two complementary approaches are pursued. One involves government/industry partnerships under the PV Manufacturing Technology (PVMaT) Project. That approach focuses on improving manufacturing processes and products, accelerating manufacturing cost reduction, and laying the foundation for increased production capacity. The second approach involves module development research to evaluate modules and module performance and suggest solutions to manufacturers’ module problems. System and market development rounds out the balanced approach pursued. The objective is to create the environment whereby system technology, user acceptance, and the PV industry can accommodate the continued expansion of PV into larger applications and markets. NREL subcontracts also support the continued influx of new ideas and highly qualified university research teams to expand the current limits of PV technology. Transferring research results into commercial products and applications in a timely and effective manner is another major activity of NREL’s PV Program.

Subcontracted R&D is a significant part of the NREL PV Program, with nearly 60% of the program’s budget allocated yearly to subcontracts. From FY 1978 through FY 1993, we awarded more than 1000 subcontracts totalling nearly $240 million out of a total BA of nearly $400 million. In FY 1993, we awarded 70 subcontracts with a total funding of $23.7 million. Cost-sharing by industry subcontractors added approximately $11.3 million to the $18.0 million in NREL funding of 35 industry subcontracts. One-half of the NREL subcontracts were with universities, with a total funding of $5.3 million. Table 1-1 shows the distribution of in-house and subcontract budgets. Figure 1-1 shows the distribution of subcontract funds by business category. Table 1-2 shows the contacts for the various NREL PV Program areas.
Table 1-1. Budget History of the NREL Photovoltaic Program

Notes: (a) Includes approximately 15%-20% for technical program management, fees, etc.
(b) Includes $9 million for photoelectrochemical cell research
(c) Significant subcontracted effort initiated in FY 1991
(d) Significant subcontracted effort initiated in FY 1992

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<td>High-Efficiency Concepts</td>
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<td>22.7</td>
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<tr>
<td>New Ideas</td>
<td>18.0&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>Subtotal (R&amp;D subcontracts)</td>
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<td>TOTAL NREL PV PROGRAM</td>
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Figure 1-1. Business category distribution of FY 1993 subcontract funds

Total subcontracts = $23.7 million
Cost-share by industry = $11.3 million (est.)

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<td>Kathy Summers</td>
<td>384-6595</td>
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<td>Kenneth Zweibel, Manager</td>
<td>384-6441</td>
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<td>Werner Luft, Manager</td>
<td>384-6452</td>
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<td>384-6402</td>
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<td>PV Module and System Performance and Engineering</td>
<td>Richard DeBlasio, Manager</td>
<td>231-1286</td>
</tr>
<tr>
<td>PV Analysis &amp; Applications Development Project</td>
<td>Roger Taylor, Manager</td>
<td>384-6432</td>
</tr>
</tbody>
</table>
1.2 Key FY 1993 Accomplishments

The following table describes some key achievements in the NREL PV Program during FY 1993. The accomplishments are grouped by the six project areas of the program. Sections 2.0 through 7.0 of this report provide further details of the in-house and subcontracted research performed under these projects.

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<tr>
<th>Research Group</th>
<th>Achievement</th>
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<tr>
<td></td>
<td>CRYSTALLINE MATERIALS AND ADVANCED CONCEPTS PROJECT</td>
</tr>
<tr>
<td>NREL</td>
<td>Researchers demonstrated the Scanning Defect Mapping System resulting in an R&amp;D 100 Award. The equipment rapidly collects information on crystallographic defects that can be correlated with other characteristics. This method provides a low-cost way to support optimization of commercial silicon wafers.</td>
</tr>
<tr>
<td>NREL</td>
<td>We achieved 29.5% efficiency in GaInP/GaAs tandem solar cell under 1-sun, global illumination. This world record is a substantial increase in the maximum PV conversion efficiency. At twice the performance of today's best commercial cells, it establishes a target for future products.</td>
</tr>
<tr>
<td>NREL</td>
<td>Researchers discovered a technique for photoluminescence analysis in silicon at room temperature using the Fourier Transformed Infrared spectrometer. This greatly reduces the cost for optical characterization of silicon by eliminating use of cryogenic helium, equipment, and time needed for conventional analysis.</td>
</tr>
<tr>
<td>NREL</td>
<td>We established computational techniques permitting first-principles calculation of systems with up to 1000 atoms. The achievement permits analysis of inhomogeneous systems including dislocations and grain boundaries.</td>
</tr>
<tr>
<td>Utah, Illinois, Johns Hopkins, North Carolina State, and South Florida Universities</td>
<td>Several universities won 3-year University Participation Program subcontract awards. Each was selected by peer review and is relatively unfettered by reporting and scheduled performance requirements. These teams are responsible for inspiring higher levels of creativity within the PV community and education of future professionals for the industry.</td>
</tr>
<tr>
<td>Massachusetts Institute of Technology (MIT)</td>
<td>MIT demonstrated silicon surface passivation by halogens (iodine and bromine) yielding recombination velocities comparable to the best oxide interface (2.1 cm/s). Control of surface recombination is needed not only for high efficiency solar cells, but also to permit rapid, reproducible electro-optical characterization of materials.</td>
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<td>Research Group</td>
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<tr>
<td>University of South Florida with Solarex and NREL</td>
<td>This cooperative research determined that conventional phosphorus and trichloroethane impurity gettering that works well in micro-electronic-grade silicon wafers is not as effective in the presence of certain structural defects common in commercial PV-grade silicon. The result clarifies the need for optimization of device fabrication processes relative to each type of silicon and continued enhancement of the understanding of process interactions with materials.</td>
</tr>
<tr>
<td>Purdue University</td>
<td>Purdue demonstrated light trapping in thin GaAs solar cell structures, a prerequisite for observation of photon recycling effects. Solar cell efficiencies 10% higher than predicted by conventional models may be achieved if the recombination-reemission (photon recycling) mechanism can be exploited.</td>
</tr>
<tr>
<td>University of Southern California</td>
<td>Researchers demonstrated low-temperature growth of GaAs with background carrier concentrations in the mid-10¹⁵ cm⁻³ range. The atomic layer epitaxy process is controlled by surface kinetics providing inherent thickness uniformity for potential in large-area deposition. The low-temperature benefit opens a wider range of candidate low-cost substrates.</td>
</tr>
<tr>
<td>NREL</td>
<td>We awarded subcontracts in the New Ideas program to Princeton University, the State University of New York at Buffalo, and Spire Corporation. They will investigate solar cells based on organic semiconductors, thin-films of silicon, and quantum-size-effect porous silicon, respectively. We also released a solicitation for high-efficiency PV research for award in FY 1994.</td>
</tr>
<tr>
<td><strong>POLYCRYSTALLINE THIN FILMS PROJECT</strong></td>
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<tr>
<td>NREL</td>
<td>In-house researchers advanced the thin-film CIS cell efficiency to world record of 15.9% (0.5-cm²-area) and 13.9% (~7-cm²-area) by a potentially manufacturable process. Demonstrated the fabrication of CIS-based devices by three different processes, with efficiencies between 14.5% and 15.9%. This shows that CIS PV can meet ambitious performance goals and the rapid progress of potentially manufacturable process.</td>
</tr>
<tr>
<td>Solar Cells, Inc.</td>
<td>Researchers fabricated a 7.7%-efficient, 7200-cm²-area (8-ft²) thin-film CdTe module by modified close-spaced sublimation. They also installed 1-kW thin-film CdTe array for testing. These results show rapid progress of a potentially low-cost, thin-film technology. The array is the world's first 1-kW system based on thin-film CdTe.</td>
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<td>Research Group</td>
<td>Achievement</td>
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<tr>
<td>Golden Photon</td>
<td>Golden Photon fabricated a 7.7%-efficient 3600-cm²-area (4-ft²) thin-film CdTe module by spraying. This module shows progress of potentially low-cost, thin-film CdTe modules by spraying.</td>
</tr>
<tr>
<td>International Solar Electric Technology (ISET)</td>
<td>ISET fabricated a 6.9%-efficient 900-cm²-area (1-ft²) thin-film CIS module. This demonstrates the potential of the two-stage process for CIS module fabrication.</td>
</tr>
<tr>
<td>Siemens Solar Industries (SSI) and NREL</td>
<td>In a collaboration with SSI, we installed a 1-kW thin-film CIS array for testing at NREL’s facilities. The typical module output is 28-30 W (4-ft²-area). This is the world’s first 1-kW thin-film CIS array.</td>
</tr>
<tr>
<td>Energy Photovoltaics (EPV)</td>
<td>EPV fabricated an 8.0%-efficient 38-cm²-area thin-film CIS submodule using Se vapor source. This is the first submodule known to be made by selenization without the use of H₂Se gas.</td>
</tr>
<tr>
<td>Boeing Company</td>
<td>Boeing fabricated a record efficiency CIS-Ga alloy cell (14.6%). These results shows that higher bandgap CIS-based cells can meet important efficiency goals.</td>
</tr>
<tr>
<td>NREL</td>
<td>We adapted a close-spaced sublimation deposition technique to fabricate CdS/CdTe devices on industrial-grade (soda-lime glass) substrates and achieved efficiencies of 10.6%. This work directly supports the CdTe industrial community, as soda-lime glass substrates are used by all major producers of CdS/CdTe devices.</td>
</tr>
<tr>
<td>University of Delaware/Institute of Energy Conversion (IEC)</td>
<td>We awarded a 5-year subcontract to IEC in recognition of their designation by DOE (in August 1992) as a University Center of Excellence in Photovoltaic Research and Education. IEC will continue their research on thin-film materials and devices in support of the PV industry.</td>
</tr>
<tr>
<td>Brookhaven National Laboratory and NREL</td>
<td>We conducted a study, in collaboration with the PV industry, on the toxicity of CIS and cadmium telluride during manufacturing and deployment of PV modules based on these materials.</td>
</tr>
<tr>
<td>United Solar Systems Corporation (USSC)</td>
<td>Researchers produced a 900-cm²-area prototype dual-junction a-Si module with reported stabilized efficiency of 9.5%. These results are the highest stable efficiency to date for this amorphous silicon module type. Progress is key to use of these modules in larger power applications.</td>
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<tr>
<th>AMORPHOUS SILICON RESEARCH PROJECT</th>
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### Research Group | Achievement
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**Solarex** | Solarex produced an 800-cm²-area prototype triple-junction a-Si module with stabilized efficiency of 8.8%. These results are the highest stable efficiency to date for this amorphous silicon module type. Progress is the key to use of these modules in larger power applications.

**NREL** | Amorphous silicon deposition was restarted and NREL researchers made the first "hot-wire" solar cell. This may lead to more stable solar cell modules.

**NREL with Industry and Universities** | The NREL PV Program established four a-Si research teams consisting of researchers from industry, universities, and NREL. The teams address issues affecting the competitiveness of today’s products. The four teams are: Wide-Bandgap Alloys, Metastability and Mid-Bandgap Alloys, Low-Bandgap Alloys, and Device Design and Interfaces.

**NREL** | We issued a Letter of Interest Solicitation for a-Si research, structured into the four team activities, to be awarded in FY 1994.

### PHOTOVOLTAIC MANUFACTURING TECHNOLOGY (PVMaT) PROJECT

**NREL** | Industry subcontractors continued research under Phase 2A (company/process-specific research). We awarded two subcontracts under Phase 3A (generic/teamed-research) to Springborn Laboratories and Spire Corporation, and evaluated proposals under the Phase 2B competition for award in FY 1994.

**AstroPower, Inc.** | AstroPower demonstrated 0.48 MW/year machine operation rate, 74% silicon feedstock use efficiency, and the first 15-cm x 45-cm solar cell in their Silicon-Film™ process. They demonstrated 8.8% efficiency on a 10-cm x 10-cm Silicon-Film™ cell.

**Energy Conversion Devices (ECD)** | ECD established the first roll-to-roll a-Si-Ge production line facility and demonstrated 7.2% stabilized efficiency on 0.37-m²-area (~ 4 ft²) triple-junction a-Si alloy modules. They demonstrated uniform, high product quality (solar cell yield > 99%) on their new continuous production line, capable of depositing the a-Si films on a 760-m long, 35-cm wide roll of flexible stainless steel.
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<th>Research Group</th>
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<tr>
<td>ENTECH, Inc.</td>
<td>ENTECH lowered production costs of several components in their concentrator systems: lens costs are down 90% (by developing continuous, prelaminated, rolled Fresnel lens), prism covers are down 75% (by improving the covers and reducing labor costs), and cell interconnects are down 80% (by improving ribbon soldering). They also eliminated solvent use in lens fabrication and developed laboratory prototype work stations for PV cell assemblies.</td>
</tr>
<tr>
<td>Mobil Solar Energy Corporation</td>
<td>Mobil Solar designed and tested a 585-nm, high-power laser dye cutting station that will increase pilot production throughput of their thin EFG octagons by a factor of two. They demonstrated the cutting feasibility of silicon wafers near the low-damage threshold.</td>
</tr>
<tr>
<td>Siemens Solar Industries (SSI)</td>
<td>SSI increased production capacity by more than 30% by improving Si ingot wire-sawing, and reduced overall manufacturing costs by 11%. SSI also saved $300,000 per year in replacement parts by switching to components with tighter tolerances in their crystal growers.</td>
</tr>
<tr>
<td>Solarex Corporation</td>
<td>Solarex improved the deposition system for multijunction, large-area a-Si modules, developed a new laser-scribing system, and installed module fabrication machinery. These changes increased processing control and reduced material costs.</td>
</tr>
<tr>
<td>Utility Power Group (UPG) with lower-tier subcontractor, Advanced Photovoltaic Systems (APS)</td>
<td>UPG completed qualification testing for candidate encapsulation materials in their POWERGLASS modules, and reduced module termination and encapsulation manufacturing costs by 50%. APS introduced three new Eureka module products and completed automation of approximately 60% of the Eureka production encapsulation line.</td>
</tr>
<tr>
<td><strong>PV MODULE AND SYSTEM PERFORMANCE AND ENGINEERING PROJECT</strong></td>
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<tr>
<td>NREL</td>
<td>We calibrated 1,532 cells (I-V under standard reporting conditions) and performed over 2,000 module measurements on the SPIRE 240A solar simulator and outdoors. These measurements were on representative cells and modules of all PV technologies being investigated at NREL and by subcontractors, as well as by the worldwide PV community.</td>
</tr>
<tr>
<td>NREL</td>
<td>Researchers established that the present EVA formulation does not have optimum concentrations of UV absorber, UV stabilizer, and thermal anti-oxidant. This knowledge will permit optimizing in FY 1994 the formulation that will maximize EVA lifetime in field-deployed modules.</td>
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<tr>
<td>Research Group</td>
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<tr>
<td>NREL with Solar Energy Industries Association (SEIA)</td>
<td>We organized a committee of PV experts to review and revise the National Electric Code Article 690. The revisions will further reduce barriers to PV integration into commercial and residential building design and installation.</td>
</tr>
<tr>
<td>NREL with USSC and Integrated Power Corporation (IPC)</td>
<td>We installed a 1.8-kW (ac) amorphous silicon PV system (USSC modules) at NREL to test roof integration of PV modules. IPC installed a 17-kW amorphous silicon system in New York City (using USSC a-Si modules). The installation demonstrates higher efficiency and more stable performance, and will improve future system designs and installations.</td>
</tr>
<tr>
<td>NREL</td>
<td>An agreement with the local utility (Public Service of Colorado) allowed interconnection of a PV system with the utility grid. The real-world test and the subsequent results are representative of actual system-interactive loads.</td>
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**PV ANALYSIS AND APPLICATIONS DEVELOPMENT PROJECT**

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<tr>
<th>Research Group</th>
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<tr>
<td>NREL</td>
<td>We completed Phase 1 of the Brazil Rural Electrification Project in a cooperative project with Brazilian utility companies and the states of Ceará and Pernambuco. 750 homes and 14 schools were provided with electricity. We also developed Phase 2 of the project, to be completed in FY 1994, which will involve 5 additional states.</td>
</tr>
<tr>
<td>DOE Golden Field Office (DOE/GO) with NREL</td>
<td>DOE/GO awarded 4 of 5 cooperative agreements under the PV:BONUS (Building Opportunities in the U.S. for Photovoltaics) project, a 5-year, $25 million (DOE) cost-shared project with industry to integrate PV into buildings. NREL provides technical support on the project.</td>
</tr>
<tr>
<td>State University of New York, Albany and the University of Delaware</td>
<td>Researchers completed a PV/utility load-matching assessment for 20 U.S. utilities (SUNY Albany) and developed a spreadsheet program to evaluate PV as a demand-side management option (University of Delaware).</td>
</tr>
<tr>
<td>NREL</td>
<td>We conducted Sunrayce '93, involving more than 2000 students in a competition to design and race solar-powered cars. Preparations for Sunrayce '95 will start in FY 1994.</td>
</tr>
<tr>
<td>NREL</td>
<td>We published <em>Photovoltaics for Municipal Planners</em> to promote the use of PV in urban areas. We initiated a quarterly technology transfer report, <em>NREL PV: Working with Industry</em>, and published <em>Solar 2000</em>, a quarterly report on outreach and commercialization activities in the DOE Office of Solar Energy Conversion. Four issues of the reports were published and distributed to more than 1200 people in the PV community.</td>
</tr>
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</table>
1.3 Technology Transfer

Consistent with DOE policy, technology transfer within NREL’s PV Program is defined as collaborative R&D with industry to aid industry in the commercialization of products or services. An underlying theme of NREL technology transfer activities is the joint work accomplished by industry researchers and NREL researchers focused on a common R&D objective. Among government laboratories, there are seven principal tools for effecting technology transfer: subcontracted R&D, cooperative R&D, industry-sponsored R&D, user facilities (at NREL), technology licenses, researcher exchanges, and information dissemination. NREL’s PV Program conducts its technology transfer primarily through three of the above: subcontracts, cooperative R&D, and information dissemination.

Subcontracts with Industry

One-half of the 70 subcontracts in FY 1993 were with the U.S. PV industry. The NREL funding of $18.0 million was supplemented by an additional $11.3 million (estimated) of cost sharing by the industry partners. The majority of the industry funding was in the PVMaT project. Technically knowledgeable NREL research managers participate in the definition, evaluation, award, and negotiation of statements of work submitted by industry researchers in competitive solicitations. Following subcontract awards, NREL subcontract managers direct and evaluate research progress through site visits to subcontractor facilities and evaluation of subcontractor deliverables in the NREL laboratories.

Cooperative R&D

NREL in-house researchers frequently perform informal cooperative R&D with their industrial counterparts working under NREL subcontracts. These interactions have been ongoing since NREL (previously SERI) PV research started in 1977. The majority of these informal cooperative R&D activities involves performance measurements and materials analyses performed with NREL's large and unique set of capabilities for PV efficiency and materials analysis. Informal cooperative R&D, as distinguished from formal cooperative research and development agreements (CRADAs), are a natural complement to NREL’s subcontracted PV program. CRADAs, as authorized by the National Competitiveness Technology Transfer Act of 1989, are formal agreements signed by the NREL Director and his industrial counterpart for the conduct of joint research projects involving both NREL and industrial researchers. Two CRADAs were signed with PV companies (AstroPower and Texas Instruments) during the latter part of FY 1993 for work to start in FY 1994, and several other CRADAs were under consideration. Informal cooperative R&D in FY 1993 included more than 10,000 measurements on PV materials, devices, and modules on properties ranging from composition and microstructure to cell and module performance. More than 150 organization from the worldwide PV community worked with NREL researchers in this fashion.

Information Dissemination

An effective traditional way to transfer technology is to report R&D results to the technical community through publications in scientific journals and presentations at technical conferences and meetings. Section 9.0 contains a bibliography of FY 1993 publications, including
subcontractor reports. During FY 1993, there were several conferences and workshops organized with the help of PV program staff members. These events included the 23rd IEEE PV Specialists Conference, SOLTECH '93, and the International Solar Energy Society Conference. Other workshops included the Photovoltaic Performance and Reliability Workshop, the PV Standards and Codes Coordination Forum, and the Workshop on the Role of Point Defects and Impurities in Silicon. These gatherings provide important opportunities for industry researchers to exchange technical information with NREL and university researchers.

1.4 Conclusions

This report reviews the in-house and subcontracted R&D activities under the NREL PV Program during FY 1993. Major PV program thrusts in FY 1993 continued to be implemented based on DOE's Photovoltaics Program Plan, FY 1991-FY 1995.

In summary, the PV Program activities involve conducting basic, applied, and engineering research; managing subcontracted R&D projects; performing research complementary to subcontracted work; developing and maintaining state-of-the-art measurement and device capabilities; performing PV manufacturing technology and module development; transferring results to industry; and evolving viable partnerships for PV systems and market development. This report describes the in-house and subcontracted R&D activities, many of which encompass close collaborations between NREL and outside researchers.

The research activities under the program are summarized under the six project areas in the following sections: Crystalline Materials and Advanced Concepts Project, Polycrystalline Thin Films Project, Amorphous Silicon Research Project, Photovoltaic Manufacturing Technology (PVMaT) Project, PV Module and System Performance and Engineering Project, and PV Analysis and Applications Development Project. The sections include a brief overview including the objectives, approaches, and some key developments. Following that are technical summaries of the in-house and subcontract activities. The subcontract sections were, for the most part, provided by the subcontractors themselves. Some were compiled by NREL project managers from various reports submitted by the subcontractors. Section 8.0 provides a list FY 1993 subcontracts, and Section 9.0 lists major research publications and subcontractor reports.
The goal of this project is to support the time-phased development of the analytical capabilities and advanced technologies needed to assist the PV industry in developing high-efficiency products for evolving markets. In FY 1993, this project addressed this goal by pursuing three objectives: i) assist the PV industry on current production problems through analysis and optimization of silicon crystal growth and post-growth cell fabrication processes, as well as continuation of technology transfer of the NREL-developed GaInP solar cell; ii) develop cost-effective materials preparation technologies for advanced thin-crystalline-films of silicon, gallium arsenide (GaAs) and other compound semiconductors for ultra-high-efficiency concentrator cells and next generations of flat-plate modules; and, iii) support fundamental and exploratory research to assure the continued source of new ideas for future products.

The silicon materials program supports eight subcontracted research teams in topics ranging from analysis of commercial silicon to clarification of the physics of point defect processes, to application of these processes in new device fabrication techniques. In-house programs include crystal growth, investigation of advanced processes, materials characterization, and development of characterization techniques. The year proved to be very productive in this area. Some of the highlights include:

The Massachusetts Institute of Technology (MIT) team led by Professor Lionel Kimerling demonstrated silicon surface passivation by halogens. Much of the recent progress in improving PV efficiencies in silicon is the result of improved passivation of electronically active defects by growth of surface oxides and treatment in atomic hydrogen. The MIT team opened new potential treatments by demonstrating that iodine and bromine can be applied to the silicon surface yielding recombination velocities comparable to the best oxide interfaces, or about 2.1 cm/s. Control of surface recombination is needed not only for high efficiency solar cells, but also to permit rapid, reproducible electro-optical characterization of materials.

The project also advanced the state-of-the-art in characterization of silicon by the invention of two new techniques that can rapidly identify impurities and defects. NREL's Center for Fourier Transformed Infrared Spectrometer (FTIR) discovered that the detector section of the instrument used for Raman spectroscopy could be used to detect the photoluminescence emission from silicon at room temperature. This greatly reduces the cost for optical characterization of silicon by eliminating use of cryogenic helium equipment and time needed for conventional analysis. NREL also demonstrated a new apparatus for identifications of grain boundaries and dislocations in silicon wafers. The Scanning Defect Mapping System received an R&D 100 Award, a recognition as one of the 100 most significant inventions for 1993 by the editors of R&D magazine. The technique relies on the difference in optical reflection characteristics that can be created for grain boundaries versus dislocations using a particular chemical etch. The equipment rapidly collects information on crystallographic defects that can be correlated with other characteristics. This provides a low-cost method to support optimization of commercial silicon wafers. Both of these inventions address the key dilemma that has faced PV scientists for decades. We have always had to choose between collecting very detailed information on a few,
potentially unrepresentative samples or collecting data from a large number of samples that may be dominated by isolated, possibly irrelevant, regions of the wafers. The speed of the new techniques now permits detailed analysis of statistically significant sample sizes at an acceptable cost.

Perhaps the most important outcome of 1993 was the coordination established among research teams at NREL, the universities, and industry directed toward advancing the understanding of commercial silicon material. For example, one collaboration drew together researches from NREL, the University of South Florida, and Solarex to study the interaction of device processing with Solarex PV wafers. They determined that conventional phosphorus and trichloroethane (TCSO) impurity gettering that works well in micro-electronic-grade silicon wafers is not as effective in the presence of certain structural defects common in commercial PV grade silicon.

The result clarifies the need for optimization of device fabrication processes relative to each type of silicon and for continued enhancement of the understanding of process interactions with materials.

Understanding how a sequence of device fabrication process steps interacts with the ensemble of defects in commercial PV silicon may not be achieved solely through analysis of the wafers after each step. Another effort in the project is to isolate particular combinations of defects. For this purpose, NREL used its float-zone facility to grow high-purity multicrystalline ingots with nitrogen or carbon. Wafers from these ingots are the processed into solar cells. The influence of a single type of defect — grain size, dislocation density, carbon or other impurity concentration — can be evaluated. In 1993, we completed studies of the influence of grain size and dislocation density in high purity materials. In 1994, the ingots with impurities added will be evaluated.

Funding in 1993 permitted only the phase-out of existing subcontracts in the second objective that addresses the development of cost-effective materials preparation technologies for advanced thin-crystalline-films of silicon, GaAs and other compound semiconductors for ultra-high-efficiency concentrator cells and next generations of flat-plate modules. The progress in the area was dramatic in spite of the shortage of new funds. The most visible result was reaching a new solar cell under 1-sun, global illumination. This is a substantial increase in the maximum PV conversion efficiency. At twice the performance of today’s best commercial cells it establishes a target for future products.

We released a solicitation for high-efficiency PV research for competitive procurement of subcontracted projects. The objective of the request for proposals (FRP) is to advance high-efficiency technologies toward prototype products through the solution of key issues and to enhance the basic scientific understanding of critical mechanisms in materials, devices, and processing. The scope of the project includes three tasks covering investigation of processes for formation of highly crystalline thin semiconductor films for flat plate modules with efficiency more than 20%, design and fabrications of concentrator devices with efficiency more than 35%, and university investigations of related fundamental issues. Projects will selected and awarded in 1994.

The two subcontracted programs that received full funding through the end of the year both
provided significant results to conclude their projects. Purdue University demonstrated light trapping in thin GaAs solar cell structures, a prerequisite for observation of photon recycling effects. Solar cell efficiencies 10% higher than those predicted by conventional models may be achieved if the recombination-reemission (photon recycling) mechanism can be exploited. The University of Southern California demonstrated low-temperature growth of GaAs with background carrier concentration in the mid-10^{15} cm^{-3} range. This was achieved using the atomic layer epitaxy potential in large-area deposition. The low-temperature benefit opens a wider range of candidate low-cost substrates. This will be particularly important for supporting the thin-film device development needs for Task 1 in the RFP mentioned above.

Although the results achieved in the first two objective areas of the program are very exciting, the most important objective of the Crystalline Materials and Advanced Concepts Program is the third, namely to support fundamental and exploratory research to assure the continued source of new ideas for future products. While the market for PV products is growing rapidly in support of remote applications in the United States, and less-developed countries the ratio of cost to efficiency is still far too high for large-scale on-grid applications in U.S. utilities. While most of the resources are focused on improving technology for a factor of two reduction to assure continued market penetration, the more than five-fold reduction needed for installations of a scale that impacts U.S. generating capacity may need some technology that is not yet discovered. In order to meet this need and protect a U.S. position in intellectual property, we completed the selection and award of subcontracts from two procurements.

First, the New Ideas Program procurement provides a forum for consideration of proposals for 2-year investigations on topics in all areas of PV. The program is intended to supplement the regular flow of new technology coming in through the main project areas and to assure that ideas that don’t fit neatly into one of the existing areas receive consideration. In 1993, we awarded three subcontracts each at a level of about $200,000 for 2-years. The winners were Princeton University, the State University of New York, and Spire corporation. They will investigate solar cells based on organic semiconductors, thin-films of silicon, and quantum-size-effect porous silicon.

Second, the University Participation made awards to Utah, Illinois, Johns Hopkins, North Carolina State, and South Florida Universities. These are subcontracts that provide 3-years of support in order to assure an adequate period for completion of thesis topics. Selected by peer review and relatively unfettered by reporting and scheduled performance requirements, these teams are responsible for inspiring higher levels of creativity within the PV community and education of future professionals for the industry. This is the only peer-reviewed program within the National PV Program. The selection process is perhaps as important as the awards that are selected in that it provides the PV research community an opportunity to identify key topics for investigation without the influence or constraints of meeting the objective already identified by existing project areas.
Objectives: Maintain and provide state-of-the-art chemical, compositional and microelectrical characterization of crystalline photovoltaic materials/devices in support of in-house researchers and industry. Understand surface and interface electronic properties of crystalline semiconductor materials as a function of chemistry and structure as determined by growth/process parameters and to determine how these surface/interface properties influence device performance and stability.

Approach/Background: Surface analysis techniques, including scanning Auger microscopy (SAM), x-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS), secondary ion mass spectrometry (SIMS) and electron energy loss spectroscopy (EELS), support the investigation of the chemical and compositional properties and electronic structure of crystalline photovoltaic materials and devices. These techniques are applied to crystalline Si, microcrystalline Si, porous Si films, H2 passivation/cleaning of Si, binary and ternary III-V’s and H2S gas/plasma passivated surfaces of crystalline III-V materials.

Status/Accomplishments: Researchers in the Surface Analysis labs coordinated activities in silicon material/device development and process development with subcontractors, i.e., Siemans, Solarex, Mobil, Crystal Systems, and TI, by providing advanced measurement and characterization support. Highlights include:

- XPS and SIMS analyses of epitaxial Si on plasma cleaned Si(100) wafers were used to evaluate a low energy plasma cleaning process for silicon wafers prior to low temperature homoepitaxial growth (collaboration with Balzers Ltd.). A low energy argon/hydrogen plasma discharge is used to remove the native oxide and hydrocarbons from the wafer surface at substrate temperatures between 100°C and 400°C. This process primarily depends on chemical etching reactions rather than physical sputtering and thus minimizes process-induced damage. Significant reduction of C and O was observed at the epitaxial Si/Si(100) interface for samples subjected to the low energy plasma precleaning process.

- SIMS was used to study Si spheres for Texas Instruments (TI) under the TI CRADA. The analyzed spheres were embedded in epoxy, cross-sectioned, polished, and coated with a thin layer of Pt to create a conductive surface. Details are proprietary.

- The diffusion of S, Ti, V, Cr, and Mo in Si was investigated using SIMS depth profiling in collaboration with Mobil Solar. Si samples were implanted separately with the five different elements and then diffused with P at 900°C for 30 min. Cr was observed to getter to the surface, V and Ti showed some redistribution while Mo showed little or no redistribution.
Similar support was provided in III-V material/device development for in-house researchers, Kopin and Spire. We also developed and implemented a sulfurization process for surface passivation of III-V semiconductors to improve device performance. Highlights include:

- SIMS was used to study dopant distributions in emitter and base layers of GaAs cell structures, AlGaAs layers grown on GaAs, AlInP2 layers, and in GaInP2/GaAs device structures.

- UPS, XPS and SIMS analyses were used to investigate H2S plasma passivation of InP(100). Results clearly show that type conversion has occurred and that the bands bend 0.5 eV resulting in a homojunction interface. Initially, the S bonds separately to both the In and the P, while at higher exposures, a stable polymeric sulfur (Sn) overlayer forms. Elevated substrate temperature results in preferential formation of In–S bonding. Passivation with H2S resulted in the best C-V characteristics for Al/SiNx/InP devices and exhibited superior stability. SIMS analyses have revealed residual S at the SiNx/InP interface in concentrations of 10^{17} – 10^{18} cm^{-3}. Some of this work was in collaboration with researchers in the Department of Electrical Engineering, University of Hawaii at Manoa and consequently a collaborative research proposal between NREL and the University of Hawaii was submitted to the Army Research Office (ARO).

**FY1993 Milestones:** 1) Provide advanced characterization of crystalline Si, microcrystalline Si, porous Si and III-V materials/devices/processes for subcontractor support, 2) Determine the effects of plasma processing on contact/junction stability and performance.

**Major Project Reports:**


**Summary Date:** December 15, 1993
Objective

In order for photovoltaic energy to be competitive with other energy sources, the cell cost must be significantly lowered from its current level. This can be accomplished by improving the efficiency of production cells from the current 13% - 15% range to 16%-18%. Achievement of this goal requires the determination of the factors limiting the efficiencies of the current cells. It also requires that we identify methods that can circumvent these limitations. To maintain the low-cost nature of the cells, the methods used to improve the cell efficiencies should not significantly increase the cell cost.

A major part of our research is aimed at assisting industry reach this goal of making silicon PV cost effective. The research objectives of our group directly address this issue by working closely with the industry. Our objectives are:

1. To develop low-cost solar cell fabrication processes that can lower the cell cost and/or improve the cell performance
2. To develop material and cell characterization techniques that can be used by the silicon industry as characterization and QA tools.
3. To assist silicon PV industry by analyzing their material, processes, and devices and providing them with feedback and suggestions for improvements. We are developing joint long-term research projects in which NREL can complement the industry research

Another task of our group is to manage the subcontracted program of Crystalline Silicon Materials Research. In this coordinated program, our group interacts strongly with the subcontractors and assists them by providing the facilities and research support of NREL.

Research Activities

In 1993, our group conducted research in a number of areas related to the crystal growth, device design and processing, and special equipment/instrumentation development. Along with other NREL capabilities that we coordinate and the special equipment developed in our laboratory, our research activities are a valuable resource for industry and foster cooperative research. Briefly, our research activities included:

1. Novel High efficiency Cell Designs and processing:
   - Light Trapping: We have performed exhaustive computer modeling of light trapping in silicon solar cells. A ray optical model was developed that includes interference for
antireflection coating design, and polarization effects. The results of light trapping by various structures such as textured pyramids, inverse pyramids, randomly rough, and slats were determined in terms of the maximum achievable current as a function of the cell thickness. The software developed for this analysis is user-friendly. The results of this analysis have been applied to develop cell designs that are now being fabricated by Optical Processing. This work is now being extended to thin film cells using a wave theory analysis.

- Optical Processing: Continued analysis of Optical Processing. It was established that Optical Processing is a photon-induced phenomenon in which the near-bandgap optical energy is preferentially dissipated near a semiconductor-metal interface to produce either a melt at the interface or alter the diffusion across it. In the melt regime, a melt initiates at the interface and propagates to either sides; the thickness of the interface melt can be controlled by controlling the energy delivered to the process wafer. Formation of the melt results in a semiconductor-metal alloy that, upon cooling, regrows epitaxially on the semiconductor. A diffusion regime is created if the energy is insufficient to produce a melt. In this regime the constituent elements diffuse across the interface with a diffusion coefficient that appears to be greatly enhanced compared to the diffusion at the wafer temperature. In either regime the interface reactions are induced by lower energies, and the rate of reactions is significantly higher than that dictated by the thermal effect alone. This effect can be exploited by a post-growth (or post-deposition) processing to favorably alter the optical and electronic properties of interfaces of a multilayer semiconductor device. Furthermore, simple optical masking can be applied to inhibit the reactions in those regions of the wafer where such reactions are not needed. Using the Optical Processing we were able to fabricate contacts with extremely low contact resistance, optically reflecting ohmic contacts, and dry texturing for light trapping in thin solar cells.

- A technique has been developed to grow very high quality thin SiO2 coatings for surface passivation. These films are grown at low temperatures (< 400 °C).

- Continued studies to investigate the mechanism of hydrogen diffusion and its passivation of defects and impurities in silicon. We have verified experimentally that diffusivity of hydrogen increases with an increase in the vacancy concentration. We have also demonstrated that the backside hydrogenation can improve commercial solar cell efficiency by about 20%.

2. Material/Cell Analysis and Equipment
One of the greatest strengths of the Semiconductor Device Process Development Lab is the unique capability to design and build equipment that can be used by PV industry for cell fabrication and process monitoring and control. In the past we have developed the Fiber Optic Solar Simulator and a manually controlled Optical Processing Furnace. During 1993 we have added two more to this list:

- Large Area Scanning Defect Mapping Systems: This system produces dislocation and grain boundary maps of commercial size wafers in about an hour. The system is easy to use and fully computer controlled. This instrument won R&D100 Award in 1993.

- Optical Furnace: We have built a computer-controlled Optical Processing Furnace that will be used for device processing. This furnace has a 6-in X 8-in process zone, and will allow us to process commercial size cells.

3. Industry support: Material and cell analyses were performed for many companies viz. Solarex, Crystal Systems, and Mobil Solar.

a) Defect analysis
• We have performed defect analysis for many companies. A facility for polishing and defect etching wafers up to 12-cm X 12-cm was developed.
• We have developed a unique Scanning Defect Mapping System to determine the defect distribution in large-area commercial substrates. This instrument can produce dislocation and grain boundary maps of 10-cm X 10-cm wafers in about an hour. The defect distribution acts as a record of thermal stresses caused during crystal growth so that the defect maps can be used to analyze growth conditions. We can also correlate the defect distribution to the minority carrier diffusion length with our Surface Photovoltage System.

b) Impurity analysis
• Through subcontracts and interactions with other in-house groups, we performed impurity analysis using FTIR spectroscopy, RBS, X-ray analysis, and SPV. Analyses were for several companies to assist them for improving crystal growth, identify sources of oxygen, carbon, and nitrogen, characterize precipitates and identify precipitation mechanisms, and Techniques for DLTS analysis were developed. It was found that MIS type of devices using a thin oxide grown at low temperatures can be used reproducibly for DLTS analysis.

c) Hydrogenation: Backside hydrogenation was performed for Solarex and Astropower.

Accomplishments in 1994

• Established a Silicon Industry Support Task under which material from industry is analyzed to determine the impurities and defects in the material and establish the performance limiting mechanisms in the material. To date, we have worked with Solarex, Crystal Systems, Mobil Solar, Siemens Solar, and Astropower.

• Developed a large-area high speed defect mapping system that determines the distribution of dislocations and grain boundaries in the wafer. This technique has been used to characterize material from solar cell industry and determine the locations of high thermal stress in the ingots.

• Designed and fabricated a new fully computer controlled Optical Processing Furnace that can process commercial photovoltaic silicon wafers (supported by Technology Maturation Fund)

• Demonstrated that Optical Processing can be applied to commercial solar cells to improve the contacts and to improve the hydrogen passivation in the bulk

• Demonstrated that back-side hydrogenation can be applied to finished cells with significant improvement (about 20%)

• Organized a Workshop on “The Role of Point Defects/Defect Complexes in Silicon Device Processing.”

• Developed a theory and computer program for the design of thin film light trapping solar cells.

• Developed a new technique for growing super high quality, low temperature SiO2 for MOS devices and solar cell passivation.

• Developed the Fiber Optic Solar Simulator for commercial license (supported by Technology Maturation Fund)
Publications

• Bhushan L. Sopori and John Benner, "Improved Silicon Photovoltaics through Defect Engineering," Submitted for presentation at the ASES Conference, April 22-28, 1993, Washington DC.
• Following papers were presented at the 23rd IEEE PVSC in Louisville, KY, in May 1993:
  - Bhushan L. Sopori, Robert Murphy, and Craig Marshall, "A Scanning Defect Mapping System for Large-Area Silicon Substrates".
  - Bhushan L. Sopori, Craig Marshall, and Doug Rose, "Optical Processing: A Novel Technology for Fabricating Solar Cell Contacts".
  - Bhushan L. Sopori, and Todd Marshall, "Optical Confinement in Thin Silicon Films".

Patents

Objective

Develop solutions to the problems inherent in the fabrication of high-efficiency, multijunction cascade solar cells.

Approach

Using atmospheric-pressure organometallic vapor phase epitaxy (OMVPE), we fabricate single crystal III-V multijunction cells. By studying and improving specific aspects of these devices, we have improved our understanding of these structures, and their ultimate efficiency.

Results

During the last year we fabricated a multijunction GaInP/GaAs photovoltaic cells with efficiencies of 29.5% at one-sun concentration and air mass (AM) 1.5 global and 25.7% one-sun, AMO. These values represent the highest efficiencies achieved by any solar cell under these illumination conditions. Three key areas in this technology are identified and discussed: the grid design, front surface passivation of the top cell, and bottom surface passivation of both cells. Aspects of cell design related to its operation under concentration are also discussed.

The GaInP/GaAs cells discussed in this report were grown by atmospheric-pressure OMVPE. The cell structure consists of a top cell of Ga_{0.52}In_{0.48}P (abbreviated as GaInP) connected in series with a low-resistivity, grown-in tunnel junction to a GaAs bottom cell, as shown in Fig. 1. The cell area is 0.25 cm^2.

The best cell produced to date for the AM1.5G solar spectrum has an energy conversion efficiency of 29.5% at one-sun AM1.5G. The current-voltage (I-V) curve, short-circuit current density (J_S), open-circuit voltage (V_OC), fill factor (FF), and top-cell band gap are given in Fig. 2(a). A different cell, optimized for the AMO spectrum, achieved a one-sun AMO efficiency of 25.7%. The device parameters for this cell are J_S = 16.4 mA/cm^2, V_OC = 2.398 V, and FF = 88.2%. The structure of this second cell differs from that of the AM1.5 cell only in that the base layer of the top cell is 0.5 µm instead of 0.6 µm to match the top and bottom cell currents for optimum efficiency.
There are three critical issues in the GaInP/GaAs tandem cell technology that have been identified in the work toward the record cells reported here: grid design, top surface passivation, and back surface passivation. Optimizing the grid design for this cell reduced the front surface contacting grid coverage from 4.9% to 1.9% of the device area without a loss in FF. This change brought about a 0.8% increase in absolute efficiency, or approximately one-third of the improvement from the previous best results. This improvement is possible only because the sheet resistance of the emitter is relatively low at 420 $\Omega$/square and because the cell operates at about half the current density of single-junction or lower band gap tandem combinations with comparable efficiencies.

A second critical issue is maintaining the quality of the top-cell front surface passivation layer, the Al$_{0.53}$In$_{0.47}$P (abbreviated AllnP) window. Devices with a poor quality window layer have markedly lower quantum efficiency in the blue end of the spectral range (corresponding to a 10% loss in top-cell current) but suffer little or no loss in $V_{oc}$. Two different solutions to this problem have been identified: (1) the substitution of disilane for hydrogen selenide as the dopant in the AllnP window layer, and (2) the use of a point-of-use phosphine purifier. The data can be explained by a decrease in oxygen contamination originating in the phosphine gas; in this scenario, the disilane is presumed to have a purifying effect by reacting with trace oxygen to form a silicon oxide that is swept out of the reactor. This hypothesis is supported by secondary ion mass spectroscopy (SIMS) results which show that AllnP doped with disilane has oxygen levels that are two to three times lower than those of AllnP doped with hydrogen selenide.

A third key area to control in this technology is the passivation of the back interfaces in both cells. Back surface field (BSF) layers are used to reduce the recombination of minority carriers at these interfaces. This recombination reduces the concentration of minority carriers in the base, which in turn increases the dark current in the device. The symptom of a BSF problem is thus a decrease in $V_{oc}$, the voltage at which the dark current becomes equal to the photogenerated current. The front surface passivation has little effect on $V_{oc}$ because almost all of the dark current is generated in the base of the cell where the minority-carrier concentrations are higher as a result of the longer minority diffusion length and lower doping. The GaInP top cell is particularly vulnerable to this effect because it is so thin, placing all minority carriers in the base only a small fraction of the minority-carrier diffusion length away from the back interface.

The BSF layer used in the GaAs cell is a thin GaInP layer. This heterojunction for lightly doped n-type layers gives very low interface recombination velocities of 1.5 cm/s. For p-type heterointerfaces, the doping levels must be around $p = 2 \times 10^{17}$ cm$^{-3}$ to achieve $V_{oc}$ values of 1.042 eV or more. When the BSF and underlying GaAs buffer layers were grown with doping level $p = 6 \times 10^{16}$ cm$^{-3}$, a three-fold increase in dark current near $V_{oc}$ was observed, $V_{oc}$ values dropped to below 1.02 eV, and devices often displayed high series resistance and nonideal I-V curves.

The BSF layer for the GaInP top cell is a layer of GaInP with a higher band gap. Because of spontaneous ordering on the Group III sublattice, the band gap of the GaInP varies with growth conditions from about 1.8 to 1.9 eV at constant composition. AlGaInP layers have been investigated as BSF layers in top cells and gave inferior performance. When incorporated into the tandem structure, however, the BSF and sometimes even the n-p junction quality was degraded by dopant memory effects and dopant diffusion that became significant at the high levels of doping used in the tunnel junction interconnect layers. Hydrogen selenide, the n-type dopant, is particularly susceptible to memory effects, in which the hydrogen selenide molecules
or some derivative compounds absorb on the reactor walls and then desorb after the source flow is stopped. To reduce this effect, the hydrogen selenide flow during tunnel junction growth is reduced while at the same time lowering the arsine partial pressure to 14 Pa (0.1 Torr). The doping levels remain high because the lower arsine pressure increases the incorporation efficiency of hydrogen selenide. Zinc, the p-type dopant, does not display strong memory effects but does diffuse readily through the growing film. When the high Zn flows needed for a tunnel junction were used, SIMS found a large accumulation of Zn in the top cell base near the n-p junction. To remedy this problem, zinc was replaced with carbon in the tunnel junction. The Se-C tunnel junction lowered the dark current in the tandem cell by a factor of six and increased the $V_{oc}$ by about 140 mV relative to tandem cells with Se-Zn tunnel junctions.

As part of developing the one-sun devices, some improvements have also been made that will be needed for the development of a concentrator cell. First, the contacting layer is modified to improve the contact resistance of the Au/GaAs interface. Adding a silicon doping spike 10 nm beneath the GaAs surface reduces the contact resistance to about $5 \times 10^{-5} \Omega \cdot cm^2$. The Se-C tunnel junction performs even better than its Se-Zn predecessor, with resistivities consistently lower than $8 \times 10^{-4} \Omega \cdot cm^2$ and peak currents greater than 300 A/cm². Finally, the Si-doped AlInP window layer has a conductivity about twice as high as that of the Se-doped layers, lowering the resistivity of the window layer beneath the grid lines to about $1 \times 10^{-4} \Omega \cdot cm^2$.

In summary, tandem GaInP/GaAs photovoltaic cells have been grown with new record efficiencies by optimizing grid pattern design, AlInP window layer growth, and BSF layers. AlInP window layer growth is found to be superior when doped with disilane or when the phosphine source gas is purified at the point of use. GaInP makes an excellent BSF layer for the p-type GaAs base provided the doping level is at least $2 \times 10^{17} \text{cm}^{-3}$. For the GaInP top cell, higher band gap GaInP passivates the back surface when a selenium-carbon GaAs tunnel junction is modified to prevent dopant memory effects and diffusion. The improvements described here represent significant progress toward the ultimate application of this technology to terrestrial power generation using concentrator solar cell modules.

Bulk semiconductor alloys grown at high temperatures are nearly perfectly random. On the other hand, many III-V semiconductor alloys exhibit spontaneous CuPt-like partial ordering when grown from the vapor phase at lower temperature. This is manifested by the splitting of the valence band maximum, a reduction in the direct band gap, the appearance of superlattice diffraction spots and altered polarizations evident in optical experiments. To quantitatively study the ordering phenomena, we developed a general theoretical method for describing alloy properties as a function of the degree of LRO composition and polarization angel. We derive from this general theory a simplified formula that describe the properties of alloys with partial LRO in terms of the properties of (i) the perfectly random alloy (LRO parameter $\eta = 0$) and (ii) the ordered superlattice ($\eta = 1$). To illustrate this general method, we first performed first-principles self-consistent band structure calculations for the fully random and the fully ordered Ga$_{0.5}$In$_{0.5}$P alloys. We then used the simplified formula and the quasicubic model to calculate the variation in the valence band splittings and the band gap reduction for partially ordered structure. Our calculated results are in very good agreement with the experimental data of Kanata et al. and Alonso et al.. Our theory provided a way to infer the degree of LRO in a sample. We find that for most MOCVD grown Ga$_{0.5}$In$_{0.5}$P alloys $\eta \sim 0.3 - 0.6$. The same theory was also applied to predict polarization-dependent optical properties, reflectance differences, and the effects of strain. Together, these provide new ways (Refs. 1-4) to detect experimentally ordering.


When partially occupied orbitals are involved, tetrahedral semiconductors tend to exhibit rather complex bond-breeding structural rearrangements. This includes reconstructions at surfaces and off-center atomic displacements in deep defects such as the GaAs:Si$^-$ ("DX") center. Here, we investigate the conditions for off-center structural instabilities (or metastability) in pure crystalline tetrahedral semiconductors such as CuCl, GaAs, and CdTe. From first-principles total energy and band structure calculations, we find that an off-center minimum, separated from the overall tetrahedral minimum by a low energy barrier, exists in a $\{111\}$ Cu displaced CuCl. This off-center minimum has a geometry analogous to that predicted for the GaAs:Si$^-$ DX center. This off-center minimum is either very weak or absent in pure II-VI and III-V compounds. These results are explained in terms of a displacement-enhanced coupling between the occupied $d$ states and the empty $s$ states. It indicates that the off-center minimum in CuCl results from a second-order Jahn-Teller effect. Our prediction of an off-center displacement leads to a number of unique physical properties: (i) $\{111\}$ cation displacements will lower the symmetry of the crystal, thus
Fig. 1. Solar cell structure. The contacting layer is removed after the grids are applied. The base thickness was varied for the two cells reported here, as noted. Dopant atom types are indicated in square brackets.

Fig. 2. I-V curve for GaInP/GaAs solar cells with 29.5% efficiency at one-sun, AM1.5G. The plus sign marks the maximum power point.
creating a dielectric anomaly. (ii) Our calculation suggest that two sets of LO phonon mode
should be observed in CuCl resulting from the two local minimum, in agreement with experiment.
(iii) The physical properties of CuCl samples are predicted to depend strongly on their thermal
history which determines the distribution of particles in the two type of energy minima. (iv)
When electron-hole recombination rate is slow, photoexcitation can enhance the population of
atoms in the off-center minima through tunneling. This is consistent with the observed photo
induced dielectric anomalies and suggests that persistent photocapacitance quenching should be
observable in CuCl. On the other hand, the absence of a double-well energy surface in our
calculation for GaAs and CdTe testifies to their stability.


Solar cells based on p-CuInSe$_2$ absorber layers ($E_g = 1.04$ eV) and n-CdS window layers ($E_g =
2.42$ eV) have developed rapidly from 5% efficiency in 1974 to about 15.9% at present. Despite
this rapid progress, the qualitative nature of the band alignment between CdS and CuInSe$_2$
remains a mystery: The traditional view is that in such cells heterojunction is formed between
p-CuInSe$_2$ and n-CdS, that the conduction band minimum (CBM) is on CdS (negative conduction
band offset $\Delta E_c < 0$) and that the valence band maximum (VBM) is on CuInSe$_2$ (positive valence
band offset $\Delta E_v > 0$). This "type-II" band alignment was thought to be essential for electron
transport from CuInSe$_2$ to CdS. This picture was initially supported by the electron affinity rule
and by early synchrotron-radiation photoemission measurements, but was sharply contradicted by
the more recent photoemission experiments for CdS/CuInSe$_2$ yielding $\Delta E_c > 0$. Uncertainties
regarding the stoichiometry of the deposited CdS film and the mechanical integrity of the
CdS/CuInSe$_2$ interface lead us to examine the internal consistency of these results. We have
performed first principles band structure calculations and find that for CdS/CuInSe$_2$ $\Delta E_v = 1.07
\pm 0.05$ eV for the relaxed interface, leading to $\Delta E_c = 0.31 \pm 0.05$ eV. This prediction compares
well with the most recent synchrotron-radiation measurements on high-quality interfaces of
CdS/CuInSe$_2$, yielding $\Delta E_v = 0.9 \pm 0.2$ and $\Delta E_c = 0.5 \pm 0.2$ eV. Both experiment and theory then
imply that the CBM and the VBM are on CuInSe$_2$ (type-I alignment). Our results indicate that
traditional view of device modelling of the performance of CdS/CuInSe$_2$ device, which uses as
input a $\Delta E_c < 0$ value and assumes heterojunction between n-CdS/p-CuInSe$_2$ must be abandoned
and the consequences of the revised value should be examined.

4. Electronic Structure Calculations for Mesoscopic Systems (S. Froyen, and A. Zunger)

Numerous semiconducting systems and devices are characterized by material properties that vary
on a scale of 10 to 100 nm. The variation can be intentional through, e.g., modulation doping,
artificially grown superstructures, etc. or it can be spontaneous as, e.g., in the lateral phase
separation and order parameter fluctuations that are observed in some (ordered) semiconductor
alloys. Such structures are often introduced into high efficiency photovoltaics, yet the theoretical
study of such systems with their large unit cells is currently beyond existing first-principles
methods. There are two possible avenues for extending our modeling capabilities to such
mesoscopic systems.

The first is to expand the computational capabilities of existing first-principles methods by porting
these methods to massively parallel computers. We began this process using a DDF grant last fiscal year and we have submitted a proposal to DOE/OER/Scientific Computing in order to provide funding for a much larger effort. The second possibility is to obtain material parameters from first-principles calculations of smaller systems and then apply these parameters in model calculations on the mesoscopic systems. Such models are known as effective mass models, Luttinger models, truncated crystal models, etc. The idea is to expand the electron wavefunction of the mesoscopic system in a small (a few states per atom), easily obtained, set of states. For a system consisting of two materials \( A \) and \( B \), the Luttinger model uses the states form material \( A \) in region \( A \) and material \( B \) in region \( B \) but ignores the fact that these states do not necessarily match at the boundaries between the regions. We have instead chosen to use a dual set of states, one from material \( A \) and one from material \( B \). The states are orthogonalized, and a subspace Hamiltonian for the mesoscopic system is constructed and diagonalized using this dual set. The operations can all be done from first principles and we therefore avoid the effective mass type approximations of the Luttinger model as well.

As an example of the type of application the new method is suited for, S. Froyen calculated the electronic structure of two (001) layers of GaAs (8-layers) in AlAs separated by \( n \) layers of AlAs. Such a structure could, for instance, be used to tune the band gap in a multiple quantum well solar cell without having to resort to alloying. The calculations are performed in a 40 layer supercell (80 atoms). It provides, in detail, the evolution of band gaps and energy levels as the separation of the two delta layers changes. A comparison with simple one-band effective-mass theory shows the effective-mass levels to be in surprisingly good agreement with the present theory. The largest discrepancy is of the order 10 meV for the heavy hole at \( n = 0 \). We conclude that a pair of GaAs "delta planes" in AlAs can form a hole trap as much as 100 meV above the AlAs VBM and the depth of the trap can be adjusted by varying \( n \). The lowest conduction band states are dominated by the AsAs \( X \) states, and although the GaAs conduction band minimum at \( \Gamma \) has a lower energy, the two states do not mix strongly and no bound state is formed. In fact, a single layer of GaAs in AlAs behaves as a conduction band barrier rather than a trap (type II behavior).

5. Surface Structure of (001) GaAs [10] (S. Froyen, and J. Northrup, Xerox PARC)

The (001) surface of III-V semiconductors in general and GaAs in particular exhibit a number of reconstructions which occur as the stoichiometry of the surface is varied. Such reconstructions are known to strongly influence the growth of solids from gas phase constituents and much effort has therefore been spent trying to determine the exact nature of the reconstructions. In collaboration with a researcher from Xerox PARC, S. Froyen has performed ab-initio calculations of the formation energies for a variety of GaAs(100) surface structures as a function of the atomic chemical potentials. They find that the surface transforms through four phases as the chemical potential varies across its accessible range. As the Ga chemical potential increases the surface transforms from an As-rich c(4x4) through two distinct 2x4 structures and finally to a Ga-rich 4x2 phase. Of these, three are structures that were either not considered or were predicted to be unstable by previous ab-initio theory. The predicted structures account for most STM observations for the c(4x4), 2x4, and 4x2 phases, and should form a solid foundation on which to interpret results. A complete account of these results is described in Ref. 10.

The objective of this research was to theoretically study the electronic and optical properties of ternary semiconductor alloys as a function of clustering-type short-range order (SRO), which is known to occur during growth. The methods used included self-consistent ab-initio and empirical pseudopotential approaches. The substitutional disorder on the cation sublattice was simulated using "Special Quasirandom Structures" (SQS), [A. Zunger, S.-H. Wei, L.G. Ferreira, and J.E. Bernard, Phys. Rev. Lett. 65, 353 (1990)], with a Warren-Cowley SRO parameter \( \alpha = 0 \) (random alloy) and \( \alpha = 1/6 \) (clustering). We found that local clustering of like cations, can lead to a reduction of the optical band gap of \( \text{Ga}_{0.5}\text{In}_{0.5}\text{P} \), \( \text{Ga}_{0.5}\text{Al}_{0.5}\text{As} \), and \( \text{Al}_{0.5}\text{In}_{0.5}\text{As} \) by \( \sim 100 \) meV. The reason is a tendency of the lowest conduction band or highest valence band state to localize on the type of clusters with the more attractive central-cell potential for electrons or holes. We obtained band gaps for the random alloys (\( \alpha = 0 \)) of 2.17 (indirect), 2.06, and 1.65 eV for \( \text{Ga}_{0.5}\text{Al}_{0.5}\text{As} \), \( \text{Ga}_{0.5}\text{In}_{0.5}\text{P} \), and \( \text{Al}_{0.5}\text{In}_{0.5}\text{As} \), respectively. Upon local clustering (\( \alpha = 1/6 \)) the gaps are 2.13 (direct), 1.93, and 1.56 eV, respectively. Note that clustering actually transforms \( \text{Ga}_{0.5}\text{Al}_{0.5}\text{As} \) into a direct-gap material. Our results suggest that control of short-range order in semiconductors could be used as an important step in band gap engineering. Furthermore, since both ordering and clustering can reduce the band gap, one has to use other experimental fingerprints (see item 1. in this section) to demonstrate that e.g., ordering takes place.


Since Si has an indirect band gap (1.13 eV), pristine Si has poor optical radiative efficiency at threshold. Despite this, recent experimental observations on porous Si have shown that Si quantum wires exhibit strong visible photoluminescence (PL) around 1.6 to 2.5 eV at room temperature with a size-dependent peak position. These observations have stimulated intense experimental activity in this field. Of particular interest here is the physical origin of the intense, blue-shifted emission. We focus on the following questions regarding Si quantum wires: (a) what causes the blue shift? --is it a quantum dot/wire confinement effect or a surface effect? (b) what causes the intense PL and (c) what are the origins of the main emitting states?

We have used the empirical pseudopotential method to study the electronic and optical properties of [001] Si quantum wires with \((110)-(110)\) square cross sections ranging from 4 x 4 to 14 x 14 monolayers (7.7 x 7.7 to 26.9 x 26.9 Å, respectively). We calculated energy levels, band gaps, oscillator strength and charge density distributions. To understand the electronic structure of these systems we calculated their properties in a step-wise process, considering first (1) "surfaceless" wires, then (2) wires with a free surface but without hydrogen and finally (3) wires with hydrogen chemisorption on the surface. Here, step (1) includes only quantum confinement effects, step (2) adds free-surface effects, and step (3) adds hydrogen chemisorption effects. We find that (i) in all cases, the band gap between bulk-like states increases as the wire size is reduced (due to quantum confinement). However, (ii) hydrogen chemisorption acts to reduce the gap (iii) Whereas the low energy states near the valence band minimum are effective-mass like, the near band gap states are decisively noneffective mass like. They can, however, be represented accurately by a linear combination of just a few off-\( \Gamma \) bulk Si states. The lowest
conduction states are pseudodirect, not direct. (iv) The calculated energy dependence of the transition lifetimes is too strong to explain the observed low-energy "slow" emission band in porous Si purely in terms of transitions in a wire. However, an alternative model which introduces a mixture of wires and boxes can account for the experimental slope.

References:


(10) "Energetics of GaAs(100)-(2x4) and -(4x2) Reconstructions", J.E. Northrup, and S. Froyen, Phys. Rev. Lett. 71, 2276 (1993).


Title: ARSINE AND HYDRIDE GENERATION FOR MOCVD FILM GROWTH

Organization: Colorado State University, Dept. of Electrical Engineering, Fort Collins, CO

Contributors: G. J. Collins, principal investigator; D. M. Shaw, Z. Q. Yu, and D. Kobobel

ABSTRACT

A simple detector has been developed using a quartz microbalance to qualitatively measure the flux of atomic hydrogen in a hydrogen beam. We have used the monitor to measure the flux of atomic hydrogen produced by two sources, a hot tungsten filament and a microwave plasma. The atomic hydrogen flux data is then compared to arsenic hydride generation from our in-situ arsenic hydride MOCVD source, where a strong correlation is found.

I. INTRODUCTION

We have developed a simple in-situ detector that is capable of qualitatively measuring the flux of atomic hydrogen generated by two atomic hydrogen radical sources. Detection employs the change in mass of a silver oxide (AgO) coated quartz microbalance to measure the changing flux of [H] species impinging on the surface provided that the atomic hydrogen sticking coefficient on the AgO surface is invariant. Herein, we measure and compare the changing [H] flux from two sources, a hot tungsten filament and a microwave plasma, versus operating conditions. We then apply this atomic hydrogen data from both H sources to the problem of determining the chemical mechanisms responsible for the gasification of solid arsenic by a hydrogen plasma. Specifically, we show a strong correlation between atomic hydrogen flux and arsenic sub-hydride (AsHx, x = 1 - 3) generation.

II. EXPERIMENTAL SETUP

A. Atomic Hydrogen Detection

We use a quartz crystal microbalance to measure the changing atomic hydrogen flux by the reduction of a known thin oxide film deposited on the balance. An AgO film is deposited on a gold electrode quartz crystal in order to overcome problems of contact oxidization encountered with conventional silver electrode sensors. When the AgO surface is exposed to an atomic hydrogen beam, the hydrogen removes oxygen from the surface by the reduction reaction AgO + 2H = Ag + H2O, decreasing the mass of the AgO film. This decrease in mass is monitored using the thickness monitor and the rate of decreasing mass is then converted to a flux of atomic hydrogen as follows.

We assume that it takes two H atoms to remove one O atom from the AgO surface, and a unity surface sticking coefficient of H on AgO. Then a H flux of $2 \times 10^{15}$ cm$^{-2}$s$^{-1}$ reduces the mass of the sensor surface $2.66 \times 10^{-8}$ gm / cm$^{-2}$s$^{-1}$. The microbalance records the rate of change of mass of the AgO surface as a function of time, and from this rate the H flux is calculated. Given all the assumptions made above, the H flux values given in this paper are not to be considered quantitative and should only be taken as qualitative figures.
Figure 2  [H] Flux from the Microwave Plasma Source vs. (a) Hydrogen Pressure and (b) Microwave Power.

B. AsHₓ Generation Via Gasification of Solid Arsenic

We have previously reported on the amount of AsHₓ generated as a function of both hydrogen pressure and microwave discharge power. Figure 3(a) and (b) summarizes these results.

Figure 3  AsHₓ Flux vs. (a) Hydrogen Pressure and (b) Microwave Power.
B. AsH_x Generation Measurements

Our AsH_x generator has been described previously when used to grow high quality epitaxial GaAs films. Briefly, a piece of solid arsenic is placed inside a 15 cm long, 1.2 cm diameter quartz tube wherein hydrogen gas (25-50 sccm) flows. No AsH_x generation occurs without a plasma. A microwave discharge is created about 2 cm upstream from the As piece using an Evenson cavity. The various atomic hydrogen species generated in the discharge (H^+, H^*, etc.) react with the solid arsenic, creating AsH_x. Our goal is to determine the relative role of each atomic hydrogen radical in the gasification process and the dominant role of any species.

III. RESULTS

A. Microwave and Hot Wire Atomic Hydrogen Generation

A hot filament is able to create from the thermal dissociation of molecular hydrogen neutral ground state atomic hydrogen without creation of any excited species. Figure 1 shows the flux of atomic hydrogen from a hot tungsten filament as a function of distance for two filament powers as measured by the quartz crystal balance. In Figs. 2(a) and 2(b), the corresponding atomic hydrogen flux from the microwave plasma source is shown. In 2(a), the microwave power is fixed at 40 W, the H_2 flow is fixed at 25 sccm, and the total pressure is varied from 250 mTorr to 2 Torr. In 2(b), the conditions are fixed at 25 sccm H_2 flow and 750 mTorr total pressure, and the microwave power was varied from 0-50 W. In both cases, the sensor is placed approximately 2 cm from the source, in order to match the conditions used in AsH_x generation as discussed below.

Figure 1  [H] Flux Created by the Hot Tungsten Filament vs. Distance from the Filament to the Sensor.
It was found that if the solid As was placed closer than about 2 cm to the discharge source of atomic H, the As was evaporated with no AsHx produced whereas if the As was placed farther than about 5 cm from the plasma, no AsHx was formed. Only in a narrow spatial region from the plasma was AsHx generated.

The hot tungsten filament atomic hydrogen generator was used in an attempt to create AsHx under conditions with a comparable flux of atomic hydrogen passed across the solid As to that from the microwave plasma. To our surprise, no measureable amount of AsHx was created indicating the importance of the excited atomic hydrogen radical species as compared to the neutral ground state species.

IV. DISCUSSION

By comparing the measured atomic hydrogen flux of Fig. 2(a) and (b) with the AsHx generated at the same conditions (Fig. 3(a) and (b)) the close correlation between the two may be seen. This correlation demonstrates that it is an atomic hydrogen species etching the As surface to produce AsHx. Further, since no AsHx is produced when the As pieces are placed too far downstream from the plasma, it is judged that the reacting [H] species gasifying the As must have a short lifetime. We are presently trying to determine this excited H species in order to determine why no AsHx is generated using the hot filament as a [H] source.

V. CONCLUSION AND FUTURE WORK

We have developed a simple, effective monitor to qualitatively measure the flux of atomic hydrogen species. Using this tool, we have shown the correlation between the [H] flux and arsenic hydride species created in our MOCVD hydride source. Further work is being done to understand the active H species responsible for AsHx generation in the plasma but why AsHx species are not created by the hot tungsten filament source of H.

REFERENCES

Title: Influence of Self-Interstitials Injected by Phosphorus Diffusion on Defect Structures and Electronic Properties in Crystalline Silicon

Organization: School of Engineering, Duke University, Durham, North Carolina


Objective

The primary objective of this research is to understand the influence of the silicon self-interstitials (injected mainly by high-concentration phosphorus diffusion) on the structure of dislocation and precipitate defects, on their electrical activity and susceptibility to hydrogen passivation, and their ability to promote gettering of metallic impurities. In this report major emphasis is placed on the controlled screw dislocation generation technique, and on the modeling of the diffusion-segregation phenomena in silicon.

Twist Boundaries in Silicon: A Model System

A change in grain boundary dislocation (GBD) configuration under point defect injection conditions, e.g., due to the Si self-interstitial supersaturation induced by high concentration P diffusion during solar cell fabrication, may be beneficial or harmful to solar cells, and may influence the hydrogen passivation efficiency of the GBD's. (001) silicon wafers can be used to produce twist grain boundaries (GB's) consisting of a square array of screw GBD's with a/2<110> Burgers vectors. For point defect injection and hydrogen passivation a controllable and reproducible structure with access within a couple of micrometers to the twist boundary is desirable. We report the results [1] of using layer transfer and hydrophobic bonding of Si wafers to produce such GB's. The specimen size is the Si wafer size, and it is highly reproducible.

In the layer-transfer/wafer-bonding method two 4" (001) Si wafers were used, one being a Si on insulator (SOI) wafer and the other a normal Si wafer. The SOI wafer has a ~2µm single crystalline Si layer on top of a SiO₂ insulator layer, with the latter being used in our experiments as a convenient etch-stop layer. The direct wafer bonding technique was used to produce the GB between the SOI layer and the front surface of the regular wafer. Figure 1 shows the wafer configurations as well as the bonding process. Prior to bonding, the native oxides on the wafer surfaces were removed by dipping the wafers in HF and then rinsing them in deionized water. Bonding was performed in a 'microcleanroom' setup developed at Duke University (Stengl et al 1988). This is a device which creates a particle-free space between two wafer surfaces, thus allowing high quality wafer bonding to be carried out in a non-cleanroom laboratory environment. On contact at room temperature, the two (hydrophobic) wafers bond to each other by Van der Waals forces between hydrogen, fluorine and possibly some water molecules adsorbed on the contact surfaces. Upon annealing at a high temperature, covalent bonding between the wafer surface Si atoms will develop. Our wafers were annealed at 1100°C for 3 h in a wet oxidation ambient, which additionally resulted in the growth of a 1,500Å thick oxide layer on the backside of each wafer, capable of withstanding 15 h of KOH-etching (15% solution) at 70°C (Fig. 1b). The backside oxide on the SOI wafer was removed by HF prior to the KOH-etching (Fig. 1c). The bulk Si of the SOI wafer was completely removed after 13 hours of KOH-etching. Subsequently, a buffered oxide etch was used to remove the 1µm thick SOI oxide, resulting in the desired GB wafer shown in Figure 1d.
Several GB wafers, with a series of rotational misorientations of \(\sim 1-3^\circ\), were prepared. Samples of each type were diffused with P at 900\(^\circ\)C using a spin-on-glass P-source material. Plan view and cross-sectional samples, from both as fabricated and P-diffused GB wafers, were prepared and examined using TEM. TEM examinations revealed that the present method of producing GB's is highly reproducible. The GB's contained not only a twist component, but also a tilt component. The presence of the latter obviously results from the original Si wafers being tilted away from the (001) orientations. Cross-sectional views offered additional confirmation of the boundary structures, and pointed out the presence of extraneous features at the interface, which were confirmed by HRTEM as being oxide precipitates.

The layer-transfer/wafer-bonding method has been found to be a reliable and convenient way of producing large area twist grain boundaries, which can obviously be extended to obtain GB's with other GBD structures. The GB's are, however, found to have structures more complicated than expected. This is partly due to the nonideal (001) wafer orientation, and partly due to the existence of oxide particles at the bonding interface. Overall, the quality of the interface as judged from high resolution studies, shows that 'microcleanroom' wafer bonding appears to be competitive with the UHV wafer bonding. It is well-known that under the influence of a supersaturation of silicon self-interstitials, screw dislocations climb into a helix structure. No difference has been found in the GBD structures before and after P in-diffusion treatment generating a self-interstitial supersaturation, most likely because the screw dislocation array is too closely spaced. Our calculations indicate that the misorientation has to be below 0\(^0\)15\(^\circ\) in order to observe helix formation. On the other hand, closely spaced screw dislocations allow the study of the change of the electrical activity of screw dislocations due to the in-diffusion of phosphorus, e.g., by using EBIC, without the development of an edge component. We believe that the presence of oxide particles at the GB can be avoided by eliminating the water rinse step in preparing the hydrophobic Si wafer surfaces and by adjusting the annealing process.

**Modeling of Diffusion-Segregation Phenomena**

Real crystals contain either inhomogeneities or are consisting of heterostructures. Therefore, diffusion of impurity atoms or point defect species occurs simultaneously with the segregation process. Due to the lack of a correct general equation, in the past the segregation process has been treated on an empirical basis. We have recently derived the diffusion-segregation equation (DSE), and it is given by

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ D \frac{\partial C}{\partial x} - \frac{C}{C_{eq}} \frac{\partial C_{eq}}{\partial x} \right],
\]

where \(C_{eq}\) is the species' thermal equilibrium concentration at position \(x\). This expression is derived on thermodynamic bases [2]. The power of this equation lies in its ability to treat the diffusion-segregation processes simultaneously, and is applicable to all cases involving such processes nomatter how complex they are, just as Fick's second law is applicable to all cases involving the diffusion process. A normalized form of this equation is

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[ D \frac{\partial C}{\partial x} - \frac{C}{k} \frac{\partial k}{\partial x} \right],
\]

which is rather convenient in the sense that, aside from \(D\), it uses only the dimensionless segregation coefficient \(k\).
We have implemented this equation into our partial differential equation solver (ZOMBIE) and proved the versatility of this approach for a variety of practical cases, some of which haven't been accessible for modeling up to now (see [2]). Just as an example, because of its direct correlation to our main concern of increasing the minority carrier lifetime in solar-grade silicon, we mention our results for the impurity gettering in Si by using the solution-stabilization mechanism. Figure 2 presents the simulation result of gettering by a 4 µm thick liquid Al layer of a fast moving impurity dissolved initially in a 400 µm thick Si wafer. It is seen that, with the simulation parameters used, the impurity concentration (normalized) in Si throughout the wafer thickness dropped by 2 orders of magnitude after a 60 s gettering annealing. For this simulation, the impurity diffusivities in both Si and the Al liquid are set to be $10^{-4}$ cm$^2$/s. This is a typical diffusivity value of a species in a liquid, and is also very close to the diffusivity values of the most prominent interstitially dissolved metal contaminant species Cu, Ni, and Fe in Si at high temperatures, e.g., 1000°C. The solubility of the impurity in the Al liquid is assumed to be $10^4$ of that in Si. This is arrived at by considering the fact that the high temperature solubilities of the aforementioned metals are in the order of $10^{16}$ to $10^{17}$ cm$^{-3}$, while the solubilities of these metals in (molten) Al is from a few to exceeding 10%, i.e., in the order of $10^{20}$ to $10^{21}$ cm$^{-3}$. At the Al-Si interface, the ratio of the impurity concentration in Al and in Si is $\sim 10^4$, which is the value of the segregation coefficient used in the simulation. As a final comment, very important from the point of view of technological applications, we mention that, for a given gettering volume at a given temperature, the solution-stabilized gettering process can be superior than the precipitation-stabilized gettering process, because in the former case gettering will occur even if the impurity concentration is below its thermal equilibrium concentration, while for the latter case the impurity thermal equilibrium value is the limit.

Conclusions

Our ability to controllably generate arrays of screw dislocations has to be improved in the near future in order to be able to perform meaningful experiments on the interaction of self-interstitials with screw dislocations. The samples obtained so far are appropriate for studying the influence of self-interstitials on the electrical activity of screw dislocations and their susceptibility to hydrogen passivation. Gettering of metallic impurities in silicon by simultaneous high-concentration phosphorus diffusion and aluminum backside deposition should be consistently modeled by the DSE. We plan to assess the role played by the supersaturation of self-interstitials injected by P-indiffusion in increasing the ultimate gettering efficiency.

References


Fig. 1 Schematic of twist boundary formation by layer transfer technique using hydrophobic wafer bonding.

Fig. 2 Simulated results of gettering a fast moving metallic impurity from the Si bulk using a wafer backside liquid Al layer. Details of the simulation are discussed in the text. Note the high gettering efficiency and gettering rate.
Title: Fundamental Research on Post-Growth Quality Enhancement Techniques in Multicrystalline Silicon

Organization: Georgia Institute of Technology, Atlanta, GA 30332

Contributors: A. Rohatgi, Z. Chen, P. Sana, J. Crotty, and J. Salami

Objective

The objective of this research is to develop a basic understanding of various post-growth quality enhancement techniques and apply them to fabricate high efficiency multicrystalline silicon solar cells. In this report major emphasis is placed on PECVD SiO$_2$/SiN deposition and forming gas anneal (FGA) for defect passivation, and Al treatment for defect and impurity gettering. These treatments have been analyzed in detail on several promising multicrystalline Si materials to provide guideline for achieving high efficiency multicrystalline silicon solar cells.

Bulk and Surface Passivation of Multicrystalline Silicon by PECVD SiO$_2$ and SiN Deposition

Three PECVD passivation schemes were investigated: a) 100 Å of SiO$_2$; b) 600 Å of SiN; and c) 100 Å SiO$_2$/ 600 Å SiN. In order to determine the best passivation scheme, experiments were conducted on high resistivity (~500 ohm-cm) FZ Si with very high bulk lifetime ($\tau_b > 15$ ms). Photoconductive decay lifetime measurements were performed after the PECVD passivation. Fig. 1 shows photoconductivity decay measurements (PCD) for the above three different passivation schemes. It can be seen that the 100Å SiO$_2$/ 600Å SiN double layer passivation give the highest effective lifetime (~10ms) or lowest surface recombination velocity ($S < 1$ cm/s). Such low $S$ value results from the combination of excellent SiO$_2$/Si interface and high positive charge density in SiN. The double layer passivation scheme was then used on various multicrystalline Si samples.

The PECVD induced bulk and surface passivation on multicrystalline materials was investigated and quantified by depositing 100Å SiO$_2$/600Å SiN films on both sides of five different multicrystalline materials, namely EFG sheet Si, Osaka regular and electromagnetic cast Si (EM), and cast Si from Solarex and Wacker. Minority carrier lifetime was measured on each sample by photo-conductive decay (PCD) before and after the passivation. In order to decouple the surface and bulk defect passivation, each sample was also measured in the air as well as in HF solution. Table I(a) shows the effective minority carrier lifetime ($\tau_{\text{eff}}$) determined by PCD measurements in air. Subscripts (uc) and (c) stand for uncoated and coated samples, respectively. It was found that $\tau_{\text{eff}}$ increased by a factor of 2.5 to 9.5 due to the PECVD SiO$_2$/SiN passivation, depending upon the multicrystalline material. It is important to recognize that the $\tau_{\text{eff}}$ includes both surface and bulk passivation effects. In order to decouple the bulk and surface passivation, each sample was also measured in concentrated HF solution before and after the PECVD passivation. HF solution is known to provide a near perfect surface passivation ($S < 1$ cm/s) for silicon, via H-Si bond formation [2]. Therefore, the PCD lifetime in HF ($\tau_{\text{HF}}$) primarily represents true bulk recombination, and the change in $\tau_{\text{HF}}$ before and after the PECVD passivation gives a very good indication of the degree of bulk defect passivation. Table I(b) shows the improvement in $\tau_{\text{HF}}$ due to the PECVD passivation for all five multicrystalline Si materials. It can be seen that with the exception of Osaka EM, all others showed significant bulk defect passivation after the PECVD deposition of SiN/SiO$_2$. The $\tau_{\text{HF}}$ increased by a factor of 1.3 to 1.7 after passivation depending upon the multicrystalline material. It is noteworthy that the bulk defect passivation efficiency is materials specific, probably due to the difference in the nature of defects in each material, but is independent of the initial bulk lifetime value $\tau_{\text{HF}}$. Since $\tau_{\text{HF}}$ is a good measure of true bulk lifetime, $\tau_{\text{eff}}$ can be expressed as:
where lifetime $\tau_e$ represents the surface recombination, which can be determined by measuring $\tau_{\text{eff}}$ and $\tau_{HF}$. The surface lifetime before and after the PECVD passivation is shown in Table I(c). The $\tau_e$ values increased by a factor of 5.5 to 23, again depending upon the multicrystalline material. Thus, the PECVD coatings provide significant bulk defect and surface passivation in multicrystalline silicon, but the degree of passivation is material specific.

Effects of Al Treatment on Multicrystalline Si Cells

In order to investigate the effects of Al gettering, n$^+$-p-p$^+$ solar cells were fabricated on 0.8 Ω-cm cast poly silicon from Osaka Titanium Corp. and 2.7 Ω-cm EFG sheet material from Mobil Solar. Cells fabricated on one half of each wafer had Al on the back side (Al-diffused cells with BSF) prior to high temperature drive-in while the other half was kept bare (Al-sintered cells with no BSF) during the 850 °C/35 min drive-in. All the cells were characterized by light and dark I-V and spectral response measurements. PC-1D device modelling was performed in selected instances to understand the Al treatment effects on cells. Table II shows a comparison of cell data for the Al-diffused and Al-sintered OTC cast poly and EFG sheet Si cells. Cast polysilicon cells showed an appreciable increase in the effective diffusion length from 183 to 245 $\mu$m and an absolute cell efficiency improvement of $\sim$ 1% due to the Al process, Table II. Model calculations showed that in the 300 $\mu$m thick OTC polysilicon cells with 183 $\mu$m diffusion length, Al BSF can only produce an efficiency improvement of $\sim$ 0.1%. Model calculations also showed that the observed 1% increase in cell efficiency in this case results from the multiple effects of Al treatment. In addition to the BSF and gettering effects, Al treatment roughens the back surface which reduces the back surface reflectance and introduces some light trapping. Detailed cell analysis showed a reduction in BSR from 85% to 69% and path length enhancement by a factor of 6 due to back texturing in these cells[3]. Model calculations revealed that Al treatment increased $J_{sc}$ by 0.2 mA/cm$^2$ due to BSF, decreased $J_{sc}$ by 0.1 mA/cm$^2$ due to reduced BSR, and increased $J_{sc}$ by 0.7 mA/cm$^2$ due to lifetime enhancement and light trapping, accounting for the observed increase of 0.8 mA/cm$^2$ in $J_{sc}$ in these cells. Table II shows the cell data for the Al-diffused and Al-sintered EFG cells. EFG cells showed much higher improvement (1.7%) in absolute cell efficiency due to the Al alloying process. This improvement is supported by a significant increase in quantum efficiency and diffusion length from 168 to 187 $\mu$m. Since the EFG cells have lower diffusion length compared to the cast poly cells, the effect of BSF is expected to be even smaller. Therefore, it is reasonable to conclude that Al gettering significantly improves the bulk diffusion length of the EFG material.

Effect of Forming Gas Anneal on Multicrystalline Si Cells

Cell fabrication involved two forming gas treatments at 400 °C, after the 850 °C Al drive-in step. This was done intentionally to enhance the beneficial effect of forming gas, if phosphorus diffused region, Al metal or Al/Si alloy layers can generate atomic hydrogen by interacting with the 10% molecular H$_2$ in the forming gas. Sintered OTC poly cells showed no change in cell performance when both first and second forming gas anneals were replaced by nitrogen anneals. However, EFG cells showed a very significant effect of FGA. In order to investigate and decouple the issue of Al gettering and FGA passivation, we fabricated 4 kinds of cells on EFG material, which is known to respond quite favorably to hydrogen passivation. Fig.2 shows that incorporation of several beneficial features in the process, namely Al diffusion, and first and second FGA for defect passivation, resulted in the best efficiency of $\sim$ 13.8-14.1%, which is comparable to good EFG cells made by intentional hydrogen ion implantation. If the Al diffusion is eliminated by fabricating Al sintered cells, then a significant drop in IQE and cell
efficiency, from 13.8 to 12.4%, is observed. This indicates that Al-induced gettering and BSF improves the EFG cell efficiency by ~1.5%, which is greater than what was observed in the case of cast material. This is not surprising since EFG material has more grown-in defects and impurities. Fig.2 shows that if the Al metal interaction with forming gas is turned off by replacing the second FGA by nitrogen anneal in the case of sintered cells, then the IQE drops further and the EFG cell efficiency decreases from 12.4 to 11.2%. This suggests that Al interaction with forming gas leads to some hydrogenation or defect passivation in the EFG material. Finally if both the 400 °C FGA anneals are replaced by nitrogen anneals, which eliminates all the beneficial effects of FGA and forming gas interaction with Al, n⁺, and p⁺ regions, then the EFG cell efficiency drops significantly to 8.6%. Thus unlike the OTC poly, EFG material benefits from both Al gettering and forming gas-induced defect passivation.

References


Table I.(a). The effect lifetime measured before and after the PECVD coating

<table>
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<tr>
<th>EFG</th>
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<td>$\tau_{\text{eff}}(\text{c})/\tau_{\text{eff}}(\text{uc})$</td>
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<td>2.5</td>
<td>9.5</td>
<td>3.9</td>
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(b). The lifetime in HF measured before and after the PECVD Coating

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<td>1.1</td>
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(c). The surface lifetime before and after the PECVD coating

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<td>9.2</td>
<td>18.9</td>
<td>18.8</td>
<td>5.5</td>
</tr>
</tbody>
</table>

where (c) and (uc) stand for coated and uncoated, respectively.
Table II. Effect of aluminum treatment on multicrystalline silicon cells

<table>
<thead>
<tr>
<th></th>
<th>Aluminum Diffused</th>
<th>Aluminum Sintered</th>
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<tr>
<td></td>
<td>$V_{oc}$ (mV)</td>
<td>$J_{sc}$ (mA/cm$^2$)</td>
</tr>
<tr>
<td>OTC</td>
<td>611</td>
<td>34.5</td>
</tr>
<tr>
<td>EFG</td>
<td>569</td>
<td>31.9</td>
</tr>
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Fig.1 The effect of three different passivation schemes on effective lifetime.

Fig.2 Measured IQE and cell data for EFG cells to decouple the effects of Al diffusion and forming gas treatment.
Introduction

Our purpose is to develop and demonstrate processes that will enhance the yield and performance of crystalline silicon solar cells. We have developed and applied an RF-PCD tool for monitor, control and process design; investigated gettering by backside Al metallization; and modeled interstitial impurity reactions. The RF-PCD tool has been applied to PV industry issues with excellent success.

Experimental Results

RF-PCD is a contactless method for measuring minority carrier lifetime in semiconductor materials. The 50 MHz probe frequency is particularly suitable for crystalline silicon where lifetimes typically range from 1 µs to 10 ms, and where a probe with a large skin depth (>500 µm) is desired. Figure 1 shows a schematic diagram of the system. A full review of work to date with this tool is presented in the NREL PV R&D proceedings [1].

A key to the accuracy and reliability of the RF-PCD measurement is reproducible surface passivation to control surface recombination velocity. We have developed an understanding of silicon surface cleaning and optimized cleaning procedures using the tool as a monitor. Figure 2 shows a typical result from high quality, NREL FZ-silicon. Lifetimes of this material range in the 1-4 ms range. Reproducibility for materials which are recleaned before each measurement is better than 2%. Results show that a final clean of 10 min in 48% HF is sufficient to yield a 2% accuracy in the measurement of a batch of "Spheral Solar™ Grade Silicon" material (TI). These silicon spheres are heavily doped and are approximately 1 mm in diameter. This method is the first to demonstrate batch monitor capability and the first to measure the quality of small silicon spheres.

A summary of applications to silicon surface cleaning was presented at the 3rd International Symposium on Cleaning Technology[2]. By using high quality FZ silicon, we have shown that RF-PCD can become a surface science probe. Figure 3 shows the increased sensitivity to surface recombination velocity for lifetimes greater than 1 ms. The measured value, $\tau_{\text{meas}}$, is a sum of the bulk and surface recombination components. When the surface recombination velocity is infinite, $\tau_{\text{meas}}$ (at $\tau_{\text{bulk}} > 1$ ms) reflects the time for minority carriers to diffuse to the surface. For lower values of $S$, $\tau_{\text{meas}}$ measures, under these conditions, $S$ in a way that can be readily deconvoluted and correlated with surface state densities (with knowledge of the minority carrier capture cross section). Table I summarizes the values of $S$ and associated surface recombination site densities, $N_s$, for
different surface preparations.

Figures 4 and 5 show results for our new environmentally preferable treatment of I$_2$:CH$_3$OH. Only $5 \times 10^{-4}$ M solution is required for optimal passivation. The results are superior to 48% HF in Si and in stability in air. We have reported the details of this passivation treatment and the relevant surface chemistry in a recent article [3].

RF-PCD as a process monitor can reveal furnace cleanliness, routinely. We have collaborated with Intel and AT&T to monitor oxidation processes, and the MIT facility to fine-tune cleaning and furnace facilities. DLTS provides a research tool for identifying contaminants which lead to yield excursions. Figure 6 shows an example of a DLTS spectrum taken on a bad lot of EFG material. The spectrum represents a superposition of Mo and Ti signals. The signals were identified and deconvoluted by direct measurement of the hole capture cross sections (Figure 7). For comparable concentrations of Ti on Mo, electron capture at Ti controls minority carrier lifetime. Using the PC-1D simulator with Mobil Solar cell parameters, we have established a direct correlation between cell efficiency and Ti concentration.

We are beginning measurement of the gettering capacity of the backside alloyed-Al contact using RF-PCD, DLTS and SEM-EBIC. Preliminary results for Si(100), 10 Ω-cm, boron-doped material show that for side-by-side heat treatments of 850C, 1/2 hour, $N_2$: τ$_{(Al)} = 91 \mu$s and τ$_{(no\ Al)} = 48 \mu$s. These results confirm that the contact getters as well as produces a back-side field. Work is continuing to identify gettered species and to optimize the alloy treatment.

Using a static lattice model we have simulated the binding, diffusion and energy levels of interstitial iron-Group III acceptor pairs. We have extensive experimental data on the system, and a theoretical foundation is needed to understand the gettering and minority carrier recombination properties of transition metals in p-type silicon. Table II compares the theoretical energy level positions with the measured values. Inclusion of charge polarization effects and local lattice relaxation yield an excellent fit. The pair energy level is the most sensitive measure of local bonding. This small anomaly for iron-boron could be due to local covalent effects or large lattice relaxation. The work is continuing with both experiments and theory.

Conclusion

Our research strategy has three components: 1) monitor and control; 2) process design; and 3) process understanding. We have developed a new, compact Radio Frequency Photoconductance Decay (RF-PCD) measurement and extended its usefulness as a process monitor to include bulk contamination, surface cleaning and surface roughness. We have developed a new, environmentally preferable clean involving I$_2$:CH$_3$OH which replaces HF as a final cleaning step. We have employed DLTS and atomistic modeling to define the equilibrium state of transition metals in silicon and their impact on cell efficiency. These initial results have involved close interaction with industry and have produced the first process monitor for the "Spheral Solar™ Grade Silicon" (Texas Instruments) material, and revealed the "killer" role of titanium when present in an EFG (Mobil Solar) material. We have worked with NREL to develop a methodology for lifetime measurement in heavily doped silicon and in very high quality float-zone (FZ) silicon. Cells have been processed in the MIT Microsystems Technology Laboratory, and improvements in materials specification and
Figure 3 The effect of surface recombination velocity ($S$) on the measured lifetime for varying bulk minority carrier lifetimes in a p-type silicon wafer.

Figure 4 The variation of lifetime with iodine concentration in methanol. The increase in lifetime is attributed to the passivation of the silicon surface with iodine.

Figure 5 Superior passivation stability of iodine versus hydrogen. The wafer is float-zone p-Si(100). $t_e$ is the time that the wafer was exposed to cleanroom air.

Figure 6 DLTS spectra taken at different conditions: 1) Long saturating pulse: tallest peaks (characteristic EFG X-Defect). 2) Short pulse: shortest peaks (Mo). 3) Difference spectrum (Ti).

Figure 7 Fraction of traps filled as a function of pulse duration for the X-Defect; the data is well described by a double exponential.
backside contact processing are evident.

References


Table I Surface recombination velocities in Si

<table>
<thead>
<tr>
<th>Surface Preparation/State</th>
<th>SRV (cm/s)</th>
<th>N (cm²)</th>
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<tbody>
<tr>
<td>Thermal Oxide</td>
<td>100</td>
<td>2x10¹¹</td>
</tr>
<tr>
<td>Si(100) in CH₃OH/Br₂</td>
<td>20</td>
<td>4x10¹⁰</td>
</tr>
<tr>
<td>Annealed (100) Oxide</td>
<td>5</td>
<td>10¹⁰</td>
</tr>
<tr>
<td>Si(100) in 48% HF</td>
<td>1</td>
<td>2x10⁹</td>
</tr>
<tr>
<td>Si(111) in 48% HF</td>
<td>&lt;0.75</td>
<td>&lt;10⁹</td>
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Table II Measured and calculated energy positions of the first, Eᵣ(1) and second, Eᵣ(2) neighbor Fe-acceptor pair

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Measured (eV)</th>
<th>Calculated (eV)</th>
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<tr>
<td>Rᵣ(A)</td>
<td>Rᵣ(Si)</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>Rᵣ(1) Eᵣ(2)</td>
<td>0.74 0.10 0.03 0.21 0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al</td>
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<tr>
<td></td>
<td>Eᵣ(1) Eᵣ(2)</td>
<td>1.01 0.20 0.13 0.25 0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ga</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.08 0.23 0.14 0.26 0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>In</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.23 0.27 0.15 0.27 0.17</td>
</tr>
</tbody>
</table>

Figure 1 Radio frequency photoconductance decay (RF-PCD) apparatus.

Figure 2 Photoconductance decay curve of Si(100) immersed in 48% HF. The insert shows the exponential fit of the decay.
The objective of this research program is to address current problems that are hindering progress towards achieving high efficiency cascade solar cells especially at high solar concentrations. During the last year our efforts were directed towards the growth p⁺-AlGaAs/n⁺-GaAs tunnel junction (Tj) using the atomic layer epitaxy technique. This Tj was then integrated in AlGaAs/GaAs cascade solar cells that can operate at high solar concentrations.

Approach

Difficulties in obtaining appropriate tunnel junctions to interconnect the cascade structure have hampered the development of multijunction concentrator cells. We present a new approach to achieve a heterostructure tunnel diode in the AlGaAs/GaAs material system with performance suitable for high solar concentrations using the ALE technique. AlGaAs was chosen for the p-type material rather than GaAs to avoid the high optical absorption of p-type GaAs. Also, the AlGaAs layer may act as a barrier to diffusion of optically generated electrons from underlying p-GaAs layer. Additionally, carbon concentrations in AlGaAs are substantially higher than in GaAs grown under the same conditions. This can be attributed to the stronger Al-C bond that leads to an enhanced incorporation of carbon into the film. High levels of background carbon concentrations can be achieved without the need of any other dopant source such as CCl₄ since C was extracted from OM sources during the ALE growth process.

Results and Discussions

The ALE reactor used in this study is based on the rotating susceptor concept. The deposition chamber is subdivided into six equally spaced compartments using quartz separators. A plan view schematic of the growth chamber is shown in Figure 1. The separators height above the substrate (Hₚ) can be finely controlled for improved confinement of reactant gases and boundary layer shearing. The chamber as modified is capable of using up to two gas inlets for each reactant gas. ALE growth was conducted upon adjusting Hₚ to 1 mm and rotating the substrate, which results in an exposure to column III reactants, then flushing by H₂, followed by an exposure to column V reactants and flushing by H₂ at a system pressure of 30 torr. MOCVD growth was also conducted without H₂ flow in the four purge injectors with Hₚ=10mm, and a susceptor rotational rate of 300 rpm to promote gas phase mixing of the reactants at a system pressure of 60 torr. ALE growth was chosen rather than MOCVD for epitaxial growth of this heavily doped heterostructure.
The tunnel diode structure was grown on n-type GaAs substrate at 650°C. It consisted of 300 Å n+-GaAs layer (n=7×10¹⁸ cm⁻³), 300 Å p⁺-Al₀.₃Ga₀.₇As layer (p=8×10¹⁹ cm⁻³) and 0.7 µm p⁺-GaAs contacting layer (p=5×10¹⁸ cm⁻³). For electrical evaluation purposes, a 0.1 µm AuGe/300 Å Ni/0.2 µm Au were deposited on the back side of the n-GaAs substrate and 0.2 µm Au was deposited on the p-GaAs top layer using photolithography techniques.

Figure 2 shows the current-voltage (I-V) characteristics of the as-grown tunnel diodes at room temperature for three different growth conditions. Diode (A) was grown using the growth conditions for maximum doping levels for p⁺ and n⁺ sides of the junction. During the growth of the n+-GaAs layer in diode (B), the exposure time of AsH₃ was increased to 2.2 sec while keeping the same V/III ratio as in diode (A) case. Diode (C) was also grown using the same growth conditions as in diode (A) case except that during the deposition of the heavily doped heterojunction interfaces, the substrate was kept under AsH₃ flux for 15 sec to establish steady state conditions and to resume abrupt interfaces.

High peak-to-valley ratio (Jp/Jv) of 10 were realized in all junctions, showing the dominance of interband tunneling, which indicates that band-gap blocking was effective in suppressing inelastic as well as elastic tunneling process. This well defined negative resistance (NR) of the diodes makes them useful in digital applications. The main features of the fabricated tunnel junctions are summarized in Table (1).

From Table (1), we conclude that the diode characteristics are sensitive to the growth conditions since the peak current density (Jp) of the tunnel junction (C) is significantly higher, and the specific resistivity (ρ) is correspondingly smaller compared to junction (A) without any decrease in the well-marked negative differential region. The high peak current density (44 A/cm²) and the low series resistance (2.2×10⁻³ Ωcm²) of diode (C) make it a good interconnector for the high and low band-gap cells in the AlGaAs/GaAs cascade structure operating at high solar concentrations. At 1000 suns operation, there will be only 44 mV voltage drop across the tunnel junction. This voltage drop is the upper limit since no corrections for the probe, metal contact, and substrate resistance are considered.

The above tunnel junction was used to connect GaAs bottom cell with Al₀.₃Ga₀.₇As top cell, to form two junctions cascade solar cell structure. Figure 3 shows the I-V characteristics at 53 suns. We found that up to 100 suns, the P⁺-Al₀.₃Ga₀.₇As/n⁺-GaAs tunnel junction does not seem to result in any appreciable deterioration in the solar cell performance.

Conclusion

In conclusion, ALE was used for the growth of p⁺-AlGaAs/n⁺-GaAs Tj that is suitable for cascade solar cells operating over 100 suns.

References

Table (1): Main features of "as-grown" tunnel diodes.

<table>
<thead>
<tr>
<th>Diode #</th>
<th>$J_p/J_v$</th>
<th>$J_p$ (A/Cm$^2$)</th>
<th>$V_p$ (V)</th>
<th>$\varepsilon$ ($\Omega$.Cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10</td>
<td>20.3</td>
<td>0.11</td>
<td>$3.2 \times 10^3$</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>27.8</td>
<td>0.12</td>
<td>$2.6 \times 10^3$</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>43.8</td>
<td>0.15</td>
<td>$2.2 \times 10^3$</td>
</tr>
</tbody>
</table>

Figure 1. Plan View Schematic of the Growth Chamber
Figure 2. Typical I-V Characteristics of a n$^+$-GaAs/p$^+$-Al$_{0.3}$Ga$_{0.7}$As Tunnel Junctions Growth at Different Growth Conditions.

Figure 3. I-V Characteristics of Al$_{0.3}$Ga$_{0.7}$As/GaAs Multijunction Solar Cell Using p$^+$-Al$_{0.3}$Ga$_{0.7}$As/n$^+$-GaAs Connecting Tunnel Junction at 53 Suns.
New III-V Cell Design Approaches for Very High Efficiency

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M. S. Lundstrom, M. R. Melloch, M. P. Patkar, M. P. Young, and G. B. Lush

1. Introduction

Single junction GaAs solar cells are currently controlled by radiative recombination, but radiative recombination is not necessarily a loss mechanism; if the cell is thick enough and if the emitted photons are confined within the cell [1]. By adopting a thin-crystalline cell approach, designed to optically confine the photons emitted by radiative recombination within the cell, lifetimes can be enhanced by an order of magnitude - or even more. Our research is directed at device physics, processing, and materials issues associated with crystalline, thin-film concentrator cells. Specific project objectives are: 1) to develop a process to produce thin crystalline GaAs cells, 2) to characterize loss mechanisms in such cells, and 3) to identify the efficiency limiting factor for such cells and to project ultimate, realizable, cell efficiencies.


During the past year, we concentrated on further development and enhancement of our thin-film device fabrication and testing facilities and techniques. The results of the thin-crystalline GaAs solar cell fabrication and characterization were presented at the 23rd IEEE Photovoltaic Specialists Conference [2]. A clear enhancement in the long wavelength internal quantum efficiency was observed and was attributed to the presence of the back surface reflector. High performance cells were not realized because of the excessive series resistance associated with the back contact, a problem now being addressed. Last year we also fabricated and characterized thin-crystalline LED's. LED's provide a convenient development tool for high-efficiency concentrator cells. Optimizing the LED's efficiency should at the same time optimize the performance of the device when operated as a concentrator cell. Finally, we also explored a novel cell design using p++ GaAs, which could produce a substantial improvement in short-wavelength photon efficiency.

2.1 Photon Recycling in GaAs LED's:

Last year's promising results from our thin-film lifetime studies [3] encouraged us to apply the design concept to thin-crystalline devices. For these studies, the peeled film technique was employed. We first used this technique to fabricate thin-film GaAs cells, but, as discussed above, the high efficiency performance has not yet been achieved. Recall also that the benefits will only be apparent under high concentration. Light-emitting diodes, however, prove to be an excellent vehicle for demonstrating the solar cell design concept. The idea is that in a thin-film LED with a reflecting back contact, emitted photons are confined so that they can be re-absorbed and re-emitted many times. The recycling process increases the probability that a photon will be emitted within the escape cone for the top surface. By increasing the number of opportunities for photon escape, the LED efficiency should be enhanced.

To examine these ideas, we fabricated n+/p double heterostructure LED's using MBE films grown at Purdue. LED's were tested while on their substrates and after lift-off and mounting on a Si wafer coated with Pd/Au/Cr. The dark I-V characteristics were
measured before and after removing the substrate, and the $n = 1$ and $n = 2$ saturation current densities were extracted by curve fitting (see Fig. 1). We found that $J_{01}$ decreased from about $9 \times 10^{-20}$ A/cm$^2$ for LED's on a GaAs substrates to about $2 \times 10^{-20}$ A/cm$^2$ for thin-film LED's. These results suggest that the bulk lifetimes were enhanced by photon recycling in thin-film LED's. The optical output of the thin-film LED's was also characterized, and the results are summarized in Fig. 2. After removal of the substrate, the optical output at a given diode current increased by a factor of five, which is very close to the factor of four reduction in $J_{01}$ and, again, indicates that the thin-film devices benefit from photon recycling. These results clearly demonstrate that fully processed thin-film devices can benefit from photon recycling.

Fig. 1. Current-voltage characteristics of the 80x80 $\mu$m$^2$ n/p LED's before and after lift-off.

2.2 Solar Cell Applications of p++ GaAs

A bare GaAs surface is poor because the native oxide creates states in the middle of the band. As a result the Fermi level is pinned at midgap, and the charged states at the surface leave a depleted region whose electric field sweeps minority carriers into the surface states. Most minority carriers generated within this region will be swept to the surface and recombine; the response to short wavelengths is degraded. Increasing the doping concentration would make the depletion region thinner so that fewer carriers would be subject to the electric field, and if the p++ region is sufficiently doped, it could act as a minority carrier mirror. For $p^{++} = 10^{20}$ cm$^{-3}$, the depletion width is $\approx 25$Å, and there would be little absorption in this thin depletion region. The elimination of the AlGaAs window and its replacement with a p++/n GaAs cell would have several processing and economic advantages.
Recently, an IBM/Purdue team demonstrated that hole concentrations of $1 \times 10^{20}$ cm$^{-3}$ could be achieved with Be doping provided the layer was grown by MBE at a substrate temperature of 350°C and subsequently annealed at 600°C in an ambient of As vapor. Even at these high doping levels, the Be was stable against inter diffusion during the anneal. With this new technology in hand a preliminary $p^{++}/n$ cell was grown and fabricated.

In this particular experiment, we decided to lower the substrate temperature from 605°C to 350°C during the growth of the final 0.6 µm of the 4 µm thick n-GaAs base layer, and the $p^{++}$ layer was grown at 350°C with Be as a dopant. The temperature change before completion of the n-GaAs layer growth was to avoid defects that would appear at the $p^{++}/n$ interface if the temperature was decreased from 605°C to 350°C during a pause in growth right after the n-GaAs layer was grown. The low temperature growth of the $p^{++}$ layer causes formation of excess As. In the subsequent high temperature anneal (at 660°C) the excess As coalesces into As precipitates which act as a source of high As pressure and produce a higher number of Be atoms on acceptor sites.

Figure 3 compares the measured IQE of our cell with that of a high efficiency cell built at Spire Corporation. The response of the Purdue cell to longer wavelengths was limited due to short lifetimes in the base of the cell, but the aim of this experiment, which was to eliminate the window layer to improve the collection at short wavelengths, was achieved. Possible remedies to the growth-related, bulk lifetime problem are being investigated.
3. Conclusions

During the past year, we demonstrated that thin-crystalline GaAs solar cells can be fabricated and that they display enhanced long-wavelength performance. Our LED studies demonstrate the benefits that can be achieved by exploiting photon recycling. At the same time, to make crystalline thin-film cells a viable technology, a number of research issues still need to be addressed. The processing of thin-films into solar cells presents a number of problems, such as the contact alloying step, which need to be addressed. There is also a need to identify the loss mechanisms in thin film cells, and improved diagnostic techniques could help. Finally, using improved fabrication processes and the knowledge gained by diagnostic studies, recombination and other losses should be suppressed and novel architecture explored so that thin-film cells can equal, or exceed the efficiencies of conventional cells.

References

Introduction

Quaternary semiconductor compounds are ideal candidates for use in cascade solar cells because the lattice constant and the bandgap of such compounds can be, within limits, independently varied. For GaInAsP lattice-matched to GaAs (and hence Ge), the bandgap spans the range from 1.42 to 1.92 eV. Junctions made from Ga_{0.84}In_{0.16}As_{0.68}P_{0.32}, with a bandgap of 1.55 eV, are both current-matched and lattice-matched with Ge junctions. Under concentrated sunlight, a Ga_{0.84}In_{0.16}As_{0.68}P_{0.32}/Ge cascade cell projects to a theoretical efficiency of greater than 40% at 100 suns [1]. Such cells are of interest for terrestrial applications.

The overall goal of the present program is to demonstrate a Ga_{0.84}In_{0.16}As_{0.68}P_{0.32}/Ge cascade cell suitable for operation under concentrated (500x) sunlight with an efficiency of greater than 32%.

Ga_{0.84}In_{0.16}As_{0.68}P_{0.32} cells are grown at RTI in a vertical, atmospheric-pressure, organometallic vapor phase epitaxy reactor at 675 °C. Trimethylgallium, ethyldimethylindium, trimethylaluminum, 100% arsine, and 100% phosphine are the precursors. Diethylzinc supplies the p-type dopant, and a 50 ppm H_2Se in H_2 mixture supplies the n-type dopant. Ge cells are grown in a low-pressure vapor phase epitaxy reactor using germane as the precursor and diborane and arsine as the p- and n-type dopants, respectively.

Results

The final cascade structure dictates the structure for each of the component junctions. Both p-on-n and n-on-p cascade configurations have been considered. Several devices have been fabricated by growing Ga_{0.84}In_{0.16}As_{0.68}P_{0.32} junctions on Ge junctions that were grown on Ge substrates. Both n-on-p and p-on-n devices have given no indication of cascade action, i.e., an active Ge junction that contributed to the V_{oc} was not observed. Alternatively, Ga_{0.84}In_{0.16}As_{0.68}P_{0.32} junctions have been grown directly on n- and p-type Ge substrates, with the idea that either Ga and In or As and P would diffuse into the Ge substrate during overgrowth, creating the appropriate active junction in the Ge. Fig. 1 is a schematic of the only structure that we have been able to grow to date using this strategy that has demonstrated cascade action. A n^+-Ga_{0.84}In_{0.16}As_{0.68}P_{0.32} buffer layer is nucleated directly on lightly doped p-Ge substrates, and then a n^{++}-Ga_{0.84}In_{0.16}As_{0.68}P_{0.32}/p^{++}-Ga_{0.84}In_{0.16}As_{0.68}P_{0.32} tunnel diode, followed by a n^+...
on-p Ga$_{0.84}$In$_{0.16}$As$_{0.68}$P$_{0.32}$ junction. During overgrowth of the Ga$_{0.84}$In$_{0.16}$As$_{0.68}$P$_{0.32}$ layers, As and P are believed to diffuse into the Ge substrate, creating the n$^+$-Ge layer. The best such cascade device to date under AM 1.5 direct illumination, without an antireflection coating, has a $V_{oc}$ of 1.18 volts, a $J_{sc}$ of 18.5 mA/cm$^2$, a fill factor of 0.75, and an active area conversion efficiency of 16.3%. (Active area efficiencies are given because of the 15% grid coverage, and because the cells are designed for use with coverglasses). The device demonstrates the feasibility of the structure.

Work has also been ongoing to improve the performance of the single junction Ga$_{0.84}$In$_{0.16}$As$_{0.68}$P$_{0.32}$ cell. The best Ga$_{0.84}$In$_{0.16}$As$_{0.68}$P$_{0.32}$ cell to date, grown on p-GaAs with a n-on-p structure (Fig. 2), has a $V_{oc}$ of 1.047 volts, a $J_{sc}$ of 22.5 mA/cm$^2$, a fill factor of 0.849, an active area efficiency of 21.8% for AM 1.5 direct illumination (Fig. 3), and an active area efficiency of 23.4% under 9.73 suns. A spectral response curve for the cell is shown in Fig. 4. There is some current loss at shorter wavelengths, possibly due to the thickness of the emitter or to the GaInP$_2$ window. The emitter thickness is constrained by the need to keep the series resistance low for concentrator applications. Use of the AlInP$_2$ window, however, should help with the blue response. The success of the Ga$_{0.84}$In$_{0.16}$As$_{0.68}$P$_{0.32}$ single junctions on GaAs indicates that if such efficient junctions can be grown on Ge, major progress will be made in achieving the goals of the program.

Conclusions

The feasibility of a Ga$_{0.84}$In$_{0.16}$As$_{0.68}$P$_{0.32}$/Ge cascade cell has been demonstrated; however, considerable work needs to be done to improve the efficiency of the device. In particular, the quality of Ga$_{0.84}$In$_{0.16}$As$_{0.68}$P$_{0.32}$ junctions grown on Ge needs to improve, as does the Ga$_{0.84}$In$_{0.16}$As$_{0.68}$P$_{0.32}$ tunnel diode interconnect [2]. Final research on the project will involve optimizing the cascade structure.

References


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<td>p-Ge substrate</td>
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<td>~ 300 µm</td>
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**Fig. 1** Schematic of the Ga₀.₈₄In₀.₁₆As₀.₆₈P₀.₃₂/Ge cascade cell.

<table>
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<tr>
<th>Metal</th>
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<td>3.5 µm</td>
<td></td>
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<tr>
<td>p++-GaInP₂</td>
<td>1 x 10^{18} cm^{-3}</td>
<td>400 Å</td>
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<td>p-GaAs</td>
<td>Buffer</td>
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<tr>
<td>p+-GaAs</td>
<td>Substrate</td>
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<td></td>
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</table>

**Fig. 2** Schematic of the Ga₀.₈₄In₀.₁₆As₀.₆₈P₀.₃₂ cell on a GaAs substrate.
Fig. 3  I-V curve for the best Ga$_{0.84}$In$_{0.16}$As$_{0.68}$P$_{0.32}$ cell grown on GaAs to date. The text gives details on the results for the cell.

Fig. 4. Spectral response curve for the cell shown in Fig. 3.
Title: Low-cost, High-efficiency Solar Cells Utilizing GaAs-on-Si Technology

Organization: Spire Corporation, Bedford, Massachusetts

Contributors: S.M. Vernon, principal investigator

Introduction

The overall goal of this research is to establish technology to produce very-high-efficiency solar cells for terrestrial photovoltaic applications. The approach involves the growth of GaAs onto Si substrates by metalorganic chemical vapor deposition (MOCVD). Efforts of prior years' research on this NREL program have resulted in achievement of a GaAs-on-Si solar cell having a verified terrestrial world-record efficiency of 21.3% at 200 suns, as shown in Figure 1. Our focus this year has been developing growth of a new material, \((GaAs)_{1-x}(Si_2)_x\), to use in a buffer structure aimed at very effective reduction of dislocations.

GaAs-on-Si Material Studies

When GaAs cells are grown on Si wafers, dislocations are generated due to the mismatch between the lattice constants of GaAs (5.65Å) and Si (5.43Å). If these dislocations thread through the GaAs cell, performance is degraded since defects act as minority-carrier recombination sites and shunt paths at the p/n junction. Judicious choice of growth techniques can significantly decrease the defect density in the GaAs cell; a primary method is to bend the dislocations parallel to the interface plane so that they no longer thread harmfully up through the cell, but run harmlessly out to the sides.

We have developed a new material, \((GaAs)_{1-x}(Si_2)_x\) alloy, as part of a strained-layer superlattice (SLS) to effectively reduce the dislocation density in GaAs on Si. Researchers at Nippon Telephone and Telegraph (NTT) Basic Research Laboratory in Japan pioneered this structure and demonstrated GaAs on Si with less than \(5 \times 10^5\) dislocations cm\(^{-2}\), at a distance of only 2 µm above the GaAs-Si interface.

It is believed that an effective way to decrease threading dislocations is to use an SLS in which the constituent materials not only differ in strain but also have a substantial difference in elastic stiffness constants. In this way it may be possible to reduce dislocation density by using both the strain and the elastic shear moduli of the individual materials. In such a situation, even when strain in the layer decreases (by defect relaxation) and becomes less effective, repulsion of dislocations arising from the mismatch of shear moduli remains strong and unaffected. A new material system that incorporates this principle is an SLS using GaAs and \((GaAs)_{1-x}(Si_2)_x\) alloy.

NTT reports that, with this structure, they have observed no dislocations over large areas of samples (= 200 µm\(^2\)), indicating that the average dislocation density in these samples is less than \(5 \times 10^5\) cm\(^{-2}\).
NTT grew \((\text{GaAs})_{1-x} (\text{Si}_2)_x\) layers by the migration-enhanced epitaxy (MEE) technique, a variation of molecular beam epitaxy (MBE). We have grown layers by MOCVD, the same growth method we use to deposit the initial GaAs-on-Si and actual solar cell layers. Growth of \((\text{GaAs})_{1-x} (\text{Si}_2)_x\) by MOCVD has not been previously reported; however, we have succeeded in depositing \((\text{GaAs})_{1-x} (\text{Si}_2)_x\) layers and \(\text{GaAs}-(\text{GaAs})_{1-x} (\text{Si}_2)_x\) superlattice structures on GaAs and on Si substrates. The alloy layers are smooth and shiny, and are single crystal, as determined by double-crystal X-ray rocking curve analysis. Thick alloy layers grown on GaAs are in tension, resulting in some cracking; the superlattice buffer uses only thin alloy layers and does not have this problem. Defect measurements have not yet been performed. Growth conditions for \((\text{GaAs})_{1-x} (\text{Si}_2)_x\) alloys are entirely compatible with growth of GaAs cells.

**Solar Cell Studies**

Spire has collaborated with researchers at Purdue University on development of thin-film GaAs solar cells using epitaxial-liftoff techniques. GaAs cells, grown and fabricated at Spire, were removed from their GaAs substrates by use of a thin AlAs release layer. Application of a metal film to the back surface increased the near-band-edge internal quantum efficiency by as much as 71%, compared with the solar cell before lift-off.

**Publications**


**References**

Figure 1  Efficiency versus concentration for a GaAs-on-Si solar cell, measured at Sandia National Laboratory. Peak is at 237 suns, where the efficiency reaches 21.3%, AM1.5D.
Theoretical Analysis of Hydrogen-Vacancy Complex Formation and Diffusion in Silicon

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Objectives

The diffusion of hydrogen has gained considerable technological importance in the past few years because of the ability of hydrogen to passivate the electrical activity of many defect centers which are electron-hole recombination centers. Although much information is already available on the diffusion of hydrogen in crystalline silicon, recent work done at NREL[1] has revealed that the diffusivity of hydrogen appears to be greater in some silicon solar cells (in particular poly-Si) than in others (notably FZ and CZ Si). Initial experiments suggest that enhanced diffusion could result from the formation and migration of vacancy-hydrogen complexes. The objectives of our work is to investigate various aspects of vacancy-hydrogen complex formation and diffusion.

Theoretical Approach

We study properties of the neutral vacancy in Si and of the following vacancy-hydrogen complexes: \{V, H\}^0, \{V, H\}^+, \{V, H_2\}^0, \{V, H_3\}^0, and \{V, H_4\}^0. The reasons for studying \{V, H\} in the neutral and positive charge states are as follows. The vacancy is known[2] to exhibit negative-U behavior, i.e., the +1 and −1 charge states, which have a single electron in a dangling bond, are unstable against the capture of an electron or hole, resulting in all electrons being paired. We therefore consider the possibility that \{V, H\}^0 captures a hole (we are dealing with p-type material) when calculating the diffusion properties of this complex. Note that \{V, H_3\}^0 could also have both charge states, but this complex is not mobile (see below) and is therefore of lesser interest for this study.

The properties calculated so far[3] are the following: (i) equilibrium geometries, (ii) electronic configurations, (iii) dissociation energies, (iv) diffusion paths, and (v) activation energies for diffusion. The goal is to establish if vacancy-hydrogen complexes form, how they look like, and whether they are mobile in Si. The activation energies of \{V, H_n\} complexes are calculated relative to that of the isolated neutral vacancy, which is known experimentally.[2] A comparison of the activation energies, e.g., of V^0 and \{V, H\}^0 obtained at the same level of theory provides direct information on the activation energy of the complex. The calculations are performed in small and large molecular clusters[3,4] using Hartree-Fock (HF) theory, ranging from approximate \textit{ab-initio} to post-\textit{ab-initio} treatments in electron correlation (MP2).[4,5] Details will be discussed elsewhere.[6]

Geometry optimizations were performed in large clusters, but the highest-level calculations (MP2) had to be done in small clusters in which only first NNs can be relaxed. A single point MP2 calculation in an 8 atom cluster requires nearly 2 GB of disk space and...
about 10 hours of CPU time on an RS6000/355 workstation. Typical energy corrections due to second NN relaxations are of the order of 0.04 eV per atom. Therefore, we do not expect to reproduce the experimental number for the activation energy of $V^0$ at the MP2 level, but to overestimate it by an amount roughly equal to the number of second NNs (12) times the energy correction mentioned above, i.e., by half an eV or so.

We are currently exploring the possibility of performing molecular dynamics (MD) simulations in large periodic supercells at the semiempirical density-functional level, using a code recently developed [7] at Texas Tech for the study of selected properties of a-Si:H. This is a new development for the research discussed here, and no result of MD simulations is available to date.

The Vacancy and Vacancy-Hydrogen Complexes

$V^0$ in Si does not consist of 4 dangling bonds in $T_d$ symmetry but undergoes a slight tetragonal ($D_{2d}$) outward distortion. This must occur since $V^0$ is an orbital triplet in $T_d$ symmetry and is therefore Jahn-Teller unstable. Our geometry optimizations are consistent with this. The result of the distortion is the formation of two long, covalent bonds. They are stretched by about 60% relative to the normal $Si - Si$ bond length, but the overlap corresponds to nearly 75% of a two-electron covalent bond. The overlap between $Si$ atoms in different pairs is nearly zero.

We optimized the geometry for all possible configurations involving the $\{V, H\}^0$ pair. The lowest-energy one has $H$ forming a two-electron $Si - H$ bond pointing toward the center of the vacancy. This leaves a dangling bond in the vacancy. $\{V, H\}^0$ has $C_1$ symmetry. The configuration of $\{V, H\}^+$ appears to be different from that of $\{V, H\}^0$. The missing electron does not simply come off the $Si$ dangling bond, leaving the rest intact. Instead, the complex reconstructs, possibly increasing the symmetry to $C_3v$. Geometry optimizations are under way.

The equilibrium configurations of the neutral $\{V, H_2\}^0$, $\{V, H_3\}^0$, and $\{V, H_4\}^0$ complexes all have $H$ inside the vacancy, tying up successive $Si$ dangling bonds: $\{V, H_2\}^0$ has one long $Si - Si$ bond and two $Si - H$ bonds, etc. This results agrees with calculations of $\{V, H_n\}$ published by other groups [8]. The calculated gains in energy from forming $\{V, H_n\}$ starting with free $H^0$ and $\{V, H_{n-1}\}$ (dissociation energies) are 3.6 eV, 3.3 eV, 3.2 eV, and 3.0 eV corresponding to $n = 1, 2, 3, \text{ and } 4$, respectively. These numbers were obtained at the ab-initio UHF level with split-valence polarized basis sets [3,6]. We checked the $\{V, H_2\}^0$ and $\{V, H_4\}^0$ values at the MP2 level and got 3.2 eV and 2.9 eV per $H$ added, respectively. For comparison, the $Si - H$ bond strength in $SiH_4$ is 3.9 eV, and the measured $Si - H$ bond strength at large $Si$ internal surfaces is 2.6 eV [9]. Our calculated values show that the vacancy is a strong trap for one to four hydrogen interstitials.

The calculated $Si - H$ bond lengths are 1.397 Å, 1.387 Å, 1.382 Å, and 1.378 Å for $\{V, H\}$, $\{V, H_2\}^0$, $\{V, H_3\}^0$, and $\{V, H_4\}^0$, respectively. This shortening is in qualitative agreement with recent infra-red absorption data [10] of the vibrational modes of $Si - H$ bonds in the vacancy, which show a steady increase in $Si - H$ frequencies with the number of $H$'s in the vacancy.
Diffusion Properties

The diffusion of $V^0$ involves one Si atom moving toward the vacancy and leaving a new vacancy behind it. The Si atom passes through the midpoint along the $<111>$ axis between the old vacancy and the new one. At that point, Si overlaps with six Si NNs. These "bonds" are about 23% longer than ideal Si – Si bonds. Because of the large amount of distortion at that point, the effects of electron correlation are large. The calculated barrier heights gets smaller as larger basis sets are used and as more electron correlation is included into the calculation. Our best value (ab-initio HF followed by MP2 corrections in electron correlation) is 1.1 eV. As discussed in the introduction, second NN relaxations could not be included in this calculation, and we do expect a correction of a few tenths of an eV. Thus, the calculated value is in reasonable agreement with the experimental one[3] (0.45 ± 0.045 eV).

We considered two possible mechanisms for $\{V,H\}^0$ diffusion (details will be published elsewhere[6]). The one that leads to the lowest barrier for diffusion is illustrated in Fig. 1. A Si atom first moves toward the vacancy (a) by about 1.3 Å. The presence of H allows it to follow an arc. This has the effect of reducing the number of stretched bonds relative to the $V^0$ case (b). This part of the diffusion is enhanced by H. The second step involves breaking and reforming a Si – H bond (b). The distance is short (about 0.5 Å), but costs more energy. Finally, a rotation (c) and final readjustment of the positions of the atoms leads to the final configuration (d), where both H and V have moved.

![Diagram](attachment:diffusion.png)

**FIG. 1:** Schematic illustration of the mechanism for diffusion of the neutral vacancy-hydrogen pair.

The barriers for diffusion of $V^0$ and $\{V,H\}^0$ calculated at the ab-initio level with MP2 corrections are shown in Fig. 2.

![Graph](attachment:barriers.png)

**FIG. 2:** Calculated barriers for diffusion of the neutral vacancy and vacancy-hydrogen pair.
The activation energy for diffusion dramatically increases with the number of $H$ atoms in the vacancy. The key incentive for a $Si$ atom to move into a vacancy is the presence of four pseudo-dangling bonds (the vacancy reconstructs, hence "pseudo"). For $\{V,H_n\}$, with $n \geq 2$, this incentive has mostly disappeared. Further, two or more $H$ atoms are already inside the vacancy, form strong $Si-H$ bonds, and prevent the motion of neighboring atoms. Our best estimate for the activation energy of $\{V,H_2\}^0$ is of the order of 7 eV. This number is comparable to the dissociation energy of both $H$'s from the complex. We doubt that $\{V,H_2\}^0$ diffuses much below the melting point of $Si$. We found no mechanism for the diffusion of $\{V,H_3\}^0$ or $\{V,H_4\}^0$. Ongoing work focuses on $\{V,H\}^+$ and on the possibility of performing molecular dynamics simulations of the diffusion process.

Conclusions

We have calculated the equilibrium geometries, electronic structures, and diffusion properties of $\{V,H_n\}$ complexes in $Si$, with $n = 0, \ldots, 4$. Some of these calculations are still under way. Our results are consistent with experimental observations whenever available. The key new result is the prediction that the $\{V,H\}$ complex is mobile in $Si$, with an activation energy comparable to that of $V^0$. The diffusion mechanism involves the motion of a bound hydrogen, i.e., is not trap-limited in the usual sense. Of course, the $\{V,H\}$ pair itself may be trapped, for example by a shallow $B$ acceptor or a self-interstitial. The latter would probably result in the release of interstitial $H$.

References

Introduction

Experiments have been performed to identify the lifetime-limiting defects in large-grained polycrystalline silicon solar cell materials, and the detrimental effects of intentionally-introduced iron. The previous report described how iron is used in our study not only as a representative transition metal impurity but also as a means of characterizing structural defects in silicon. This characterization method utilizes iron precipitation kinetics to identify the approximate concentration of heterogeneous precipitation sites. It has been employed previously to study internal gettering processes in Czochralski silicon.[1,2]

Our results this year have provided direct evidence for an unidentified intragranular defect which acts as a precipitation site for iron, thus increasing the precipitation rate. This defect has previously been observed [3, 4]. However, our work has shown a relationship between minority carrier lifetime and iron precipitation rate which suggests these unidentified intragranular defects lower minority carrier lifetime.[5] Additionally, our results indicate metallic impurities decorate this defect even in the presence of a standard gettering mechanism and subsequently lowers carrier lifetimes.

Experimental Results

In the previous annual report we described how the iron precipitation rate in two EFG samples was strongly related to their diffusion length before iron introduction. We have extended our measurements to a greater variety of EFG samples, as well as cast polycrystalline material made by Bayer, Czochralski material from Siemens Solar, and float-zone reference material.

The complete set of materials characterized with iron precipitation kinetics measurements include Mobil EFG samples ranging in original diffusion length from 10 to 45µm, a set of Bayer cast polycrystalline silicon samples with diffusion lengths ranging from 65 to 145µm, two Siemens Solar Czochralski silicon samples, as-grown and phosphorus diffused, with diffusion lengths 72 and 106µm, and a float zone reference sample with a diffusion length ~ 600µm. Diffusion lengths were measured with the surface photovoltage (SPV) technique. Each sample was iron-diffused at 1050°C for an hour, and quenched to room temperature in ethylene glycol. Precipitation kinetics were observed with DLTS. The relationship between iron precipitation rate and as-grown minority carrier diffusion length was determined in all the materials in order to examine the carrier recombination properties of defects which act as iron precipitation sites. The results are shown in Fig. 1, in which iron precipitation rate (1/time constant) is plotted versus carrier recombination rate (1/L^2) in the as-grown materials. Clearly, those materials with lower diffusion lengths also contain higher structural defect densities. This relationship has been shown for EFG material alone [5] but appears to hold true for a variety of other solar cell materials as well. Since dislocations are known to accelerate iron precipitation,[2] it is important to determine how much of the observed iron...
precipitation in polysilicon material is attributable to dislocations and how much to other intragranular defects. (Grain boundaries are negligible in this large-grained material.) Considering Mobil sample #25 is dislocation-free, one may conclude that although dislocations increase the rate of iron precipitation in EFG and other materials, unidentified intragranular defects are also present in dislocation-free EFG material which act as iron precipitation sites and lower the material's as-grown minority carrier diffusion length. The precipitation effects of each defect are roughly additive. Dislocation densities in the other materials were insufficient to greatly affect the precipitation kinetics. The results of Siemens Czochralski and Bayer cast polycrystalline silicon indicate structural defects, absent in float-zone silicon, reduce minority carrier diffusion length in both materials.

In order to determine how detrimental the unidentified intragranular defect could be to carrier lifetime and solar cell performance in accidently contaminated and processed cells, an additional experiment utilizing phosphorus gettering was performed. EFG material with as-grown diffusion lengths of 114 and 20 µm were intentionally contaminated with $2 \times 10^{13}$ cm$^{-3}$ of iron and then subjected to a standard phosphorus gettering treatment designed to remove the unwanted iron. Diffusion lengths were measured with SPV at each step. Since the high diffusion length material was dislocation-free, the experiment was expected to reveal the ability of the unidentified intragranular defects to act as transition metal precipitation sites even in the presence of a proven gettering mechanism. Details of the experiment are given in our August MTSR. The results, shown in figure 2, clearly portrays the inability of the phosphorus gettering to negate the affect of iron on diffusion length in both samples. Since DLTS did not detect any residual iron or other point defect in either sample, these results indicate the iron has precipitated at the unidentified intragranular defects in the dislocation-free sample and, consequently, has drastically reduced the material's diffusion length. This implies the intragranular defects affect on diffusion length is increased with impurity decoration and phosphorus gettering is not adequate to entirely remove iron from these defects.

Discussion and Future Work

Iron precipitation kinetics have proven a useful technique to detect the presence of structural defects in polycrystalline silicon solar cell material. The degree to which these defects reduce diffusion length, and ultimately the solar cell efficiency, is indicated by the results shown in Fig. 1. It is clear that those materials which have low diffusion lengths contain high densities of intragranular structural defects that increase the rate of iron precipitation. These defects are proposed to be the lifetime-limiting defects. In addition, the diffusion length values of dislocation-free EFG polysilicon and Bayer cast polysilicon indicate the unidentified intragranular defect observed in [3, 4, 5] is responsible for this upper limit as-grown diffusion length in polysilicon. (In none of the EFG samples examined was there a quantity of dissolved transition metals or other identifiable point defects sufficient to account for the measured low diffusion length. In the cast, Czochralski, and float-zone samples, such a concentration approaches or is below the DLTS detection limit.) The results shown in figure 2 indicate this unidentified intragranular defect has the ability to lower a material’s diffusion length via transition metal decoration even in processed material. This suggests a dependence of minority carrier diffusion length upon the level of decoration of the precipitation sites (unidentified intragranular defects). Additionally, it is possible that the recombination activity of the intragranular defects before intentional iron contamination results from a pre-existing low level of transition metal contamination. We can then postulate that the lifetime-limiting defects in EFG silicon, and perhaps all of these materials, are structural defects.
decorated by small amounts of transition metals present during crystal growth.

We will soon test both of these hypotheses, by performing similar experiments with lower levels of iron contamination (progressively lower in-diffusion temperatures), and by attempting to detect residual transition metals in as-grown materials. The latter task will require sophisticated heating and cooling capabilities: rapid optical heating to prevent contamination from outside sources, and rapid cooling to prevent re-precipitation during sample cooling. To this end we are currently assembling a rapid thermal annealing apparatus with quenching capability, which we will soon apply to all materials previously studied.

Summary

By observing interstitial iron precipitation kinetics we have found that low-diffusion length polycrystalline silicon contains higher densities of structural defects that increase the rate of interstitial iron precipitation compared to high-diffusion length materials. This trend is observed among Mobil EFG material, as well as among all types of single- and polycrystalline silicon. Our results indicate an unidentified intragranular defect limits the diffusion length in polycrystalline and Czochralski silicon when compared to Float Zone silicon. Additionally, we observe this defect can significantly lower diffusion length values even in processed material. The degree to which these defects are decorated with transition metals after growth and the dependence of final diffusion length on contamination level will be the subject of our future work.
Figure 1. Interstitial iron precipitation rate versus carrier recombination rate in as-grown material. (Mobil EFG, Bayer cast polycrystalline, Siemens Czochralski, float-zone control)

Figure 2. Minority carrier-diffusion length of Mobil Solar EFG at various stages of treatment.
References

Title: Optimization of Gettering Processes for Photovoltaic Silicon

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Contributors: L. Jastrzebski, principal investigator; S. Ostopenko, W. Henley, D. Schielein, and J. Lagowski

Objective

This effort is focused on the development and optimization of gettering procedures whose application will enhance the quality of low-cost PV poly-silicon.

Technical Approach

The results of phosphorous (P), chlorine (Cl) (high temperature) and acoustic (low temperature) gettering will be discussed. Poly-crystalline Si (62 samples, 100 cm² each) grown by casting, HEM and EFG were used. The measurements of the diffusion lengths (L) along with Fe and Cr concentrations prior to and after gettering were used to evaluate the effectiveness of the gettering. A commercial SPV system was used for the measurements. The homogeneity of the poly-silicon samples was evaluated from high density maps of L (1500 points per sample) and Fe and Cr concentration from 177-point maps. For details of the measurement procedure, and the processing conditions, see last year's report.

Results of Cl and P Gettering

Figure 1 shows examples of an L scan (in HEM material) together with the Fe concentration measurements. The Fe concentration is usually the highest in regions with high L and smallest in grains with low L. It should be emphasized that the SPV technique measures Fe and Cr which is dissolved in the Si (in non-precipitated form). In the EFG samples, there is a clear correlation between low L regions and some grains. In contrast to the EFG material, samples prepared by the casting and HEM methods indicate no correlation between grain size or location and L values. A histogram of L value distribution measured in the samples grown by different methods is shown in Figure 2. The L values range from 10 μm to 260 μm with the center of distribution around 125 μm. The maximum Fe and Cr concentrations, observed in a few limited areas of some of samples, reaches 10^{14} cm^{-3}. An average Fe concentration is in the range of 10^{12} to 10^{13} cm^{-3} (see Figure 3).

Similar results were obtained for P and Cl gettering. The effects of Cl gettering on L and Fe in various regions of the sample are shown in Figures 1 and 3. Figure 3 shows the statistical distribution of L and Fe concentration measured prior to and after gettering. This data represents measurements of about 2500 points performed on samples grown by all three methods. No significant differences in behavior were observed for the investigated growth methods. The gettering improves the average diffusion length value but does not affect L in the regions with the lowest L values which is clearly visible in the linear scan of L and Fe prior to
and after gettering (Figure 1). The gettering reduced the Fe concentration by about an order of magnitude (Figure 3) as the mean decreased from $7 \times 10^{12}$ cm$^{-3}$ to $8 \times 10^{11}$ cm$^{-3}$ and the maximum value from $3 \times 10^{14}$ cm$^{-3}$ to $2 \times 10^{13}$ cm$^{-3}$. Prior to gettering, the Fe-B concentration was limiting the L values for approximately 616 of the measured points (about 25% of the total points) while after gettering this number was reduced to 87 points (about 3%).

**Approach: Ultrasound Treatment in Poly-Silicon (Acoustic Gettering)**

Ultrasound treatment (UST) applied to a semiconductor can affect the properties of point and extended defects. We initiated an investigation of the effects of UST on minority carrier diffusion lengths in poly-crystalline Si. External piezoelectric transducer operated at resonance frequency was used as a source of US vibrations. UST parameters such as: applied ac voltage (2 to 40 volts); holding time (10 to 90 minutes); temperature (20°C to 100°C) and frequency were adjusted to optimize the effect of UST.

The line scans of L before and after UST are depicted in Figure 1. The strongest effect of UST on L is observed at 50°C to 65°C. The largest effect of UST is found in the region with relatively low L value (see Figure 4). The relative variations of L, $\Delta L/L$, induced by UST in a different sample, are shown in Figure 5a. Three subsequent UST were applied to the sample: UST1 (40 volts/30 minutes/40°C/38 KHz); UST2 (55 volts/30 minutes/60°C/39 KHz); and UST 3 (32 volts/80 minutes/40°C/38 KHz). The UST causes either an increase or decrease in L which is specific to a particular region of the wafer (see Figure 5a). The value of $\Delta L/L$ is a function of UST parameters. The stability of the UST effect was investigated. The $\Delta L/L$ values after 76-hour relaxation at 18°C and subsequent 10 minute annealing at 80° are presented in Figure 5b. A negligible relaxation occurred in the region with largest increase of L. The increase of L after relaxation of UST is observed in particular for $\Delta L/L < 0$.

**Conclusions**

The results indicate that poly-silicon is very inhomogeneous and contains regions with low L. There is a small amount of dissolved Fe and Cr in these low regions. In the region with large L, a significant amount of dissolved Fe and Cr has been detected ($10^{12}$ to $10^{13}$ cm$^{-3}$). These concentrations could be sufficiently high to impose a limit on L.

Gettering by Cl or P significantly improves L and reduces Fe and Cr concentration in the good regions, but has only slight effect on L in the bad regions. These results appear to indicate that the recombination centers controlling lifetime in the bad regions are most likely introduced by decorated (?) crystallographic defects and formed during the growth.

The significant improvement of L in the low L regions has been observed during UST at 60°C (acoustic gettering). These initial results are very promising although the observed phenomena is rather complicated and, at this stage, the physical mechanism is not understood. These finds need to be explored so the UST process can be optimized. The results of high temperature gettering indicate that improvement of the low L regions requires restructuring of the crystallographic defect structure which can be achieved during RTA. In the next year, in addition to UST, we plan to investigate the effects of RTA with and without Al gettering.
Figure 1. Line scan of L and Fe prior to and after Cl gettering.

Figure 2. Histogram of L distribution in sample grown by various methods.

Figure 3. Effect of Cl gettering on L and Fe in PV silicon.
Figure 4. Line scans of L in poly-silicon before and after UST.

Figure 5. Line scans of $\Delta L/L$ for three different UST (a) and subsequent relaxation (b).
Program Outline

The objective of this program is to explore and develop a low temperature, large scale epitaxial process for high efficiency solar cells based upon atomic layer epitaxy (ALE). ALE has the potential for high throughput, layer thickness control and uniformity based upon the inherent saturated surface reactions involved in the process. We have previously shown that the growth rate in atmospheric pressure, thermally driven ALE is limited by the maximum temperature attainable before homogeneous gas phase reactions dominate the process and preclude the achievement of saturated monolayer growth. In this program we are exploring the use of vacuum ALE (VALE) as an alternative approach for achieving usable growth rates and high throughput. The program is structured in two phases. In the first phase, we measured the fundamental thermal and photoassisted surface reaction rates involved in the growth of GaAs using TMGa and a variety of As sources. Based upon these results a decision was made that the vacuum ALE approach was a viable approach to use for the growth of GaAs and related compounds. The second phase will concentrate upon developing VALE for the growth of high efficiency solar cells. Issues such as materials quality, reactant utilization, and throughput will be examined.

Program Results

The basic principle of VALE is to grow material in a high vacuum environment such that the mean free path of particles is increased and gas phase decomposition is minimized. Under these conditions the window for ALE growth (i.e. the range of growth parameters) will be extended. The V-ALE reactor consists of a UHV process chamber, a sample entry chamber and gas handling systems. Both of the chambers are pumped with turbomolecular pumps. The gas handling system is designed so that a reservoir is maintained near constant pressure by balancing a steady-state inlet of reactants controlled with dosing valves with the time average of the pulsed outlet of the reactants injected into the reactor. The exposure level or flux of reactants onto the substrate is controlled by the product of the conductance of orifices and the pressure in the reservoir; the exposure time is the open duration of a switching valve.

Fig. 1 shows the dependence of the growth rate on the TMGa exposure level and exposure time. A cycle is the sequence of TMGa exposure, pumping, TBAs exposure and pumping. At a constant TMGa exposure level of 0.086 µMole/sec, the growth rate increases with the exposure time up to one monolayer per cycle and then saturates at that level for durations up to four seconds. Distinct saturation is also shown with the variation of the TMGa exposure level. The data indicate a clear self-limiting...
decomposition of TMGa and also show that the control of the growth thickness at atomic scale is not a difficult task in VALE.

The surface morphology of VALE grown GaAs is mirror-like and no gallium droplets are found even for long exposure time or high exposure level of TMGa. These observations imply that the gas phase decomposition of TMGa is significantly suppressed, and the surface reaction is the dominating process in VALE. The shortest exposure time of TMGa is the result of fast switching of the gas handling system. This capability allows the V-ALE apparatus to achieve higher growth rates than other high VALE systems\textsuperscript{1-3}. Growth rates of 0.1 µm/hr are routinely employed. These can be increased by increasing the substrate temperature and the reactants' exposure level.

The dependence of growth rate on TBAs exposure also shows distinct self-limiting decomposition of TBAs in terms of the exposure time and exposure level. The TBAs exposure level for monolayer growth is ten times of the TMGa exposure level, which implies that the reaction of TBAs on Ga surfaces is slower than TMGa on As surfaces. The mechanism of the self-limiting decomposition of TBAs is probably due to the low sticking coefficient of As on As surfaces\textsuperscript{4}. The required exposure time of TBAs for monolayer growth is much shorter than the reported value of using AsH\textsubscript{3} under similar conditions\textsuperscript{1}.

The temperature window of the monolayer growth is also an important issue for ALE growth. Fig. 2 shows the widest temperature window reported in high vacuum ALE growth. The growth rate drops below one monolayer per cycle when the temperature is less than 500°C or higher than 570°C.

All of the grown films are p-type, and the carrier concentration varies from \(10^{17}\) to \(10^{19}\) cm\textsuperscript{-3}. Carbon is the likely impurity. Carbon incorporation has been reported in CBE and ALE growth\textsuperscript{1, 5, 6} A detailed mechanism is still under investigation, but several groups point out that the methyl radicals, supplied by decomposed TMGa on the GaAs surface, may play an important role on the carbon incorporation\textsuperscript{7, 8} In V-ALE growth the hole concentration varies with the growth conditions. Figs. 3 shows the dependence of the hole carrier concentration on TBAs exposure level. The hole concentration saturates when the TMGa exposure level is more than enough for monolayer growth. However, for less-than-monolayer growth, the hole concentration decreases dramatically as the TMGa exposure level decreases. These two different behaviors indicate that the carbon incorporation must be related to the population of carbon species on the GaAs surface during the TMGa exposure. As TBAs exposure increases, the hole concentrations decreases. This observation indicates that TBAs helps reduce the carbon incorporation. The growth of the lowest hole concentration, \(6 \times 10^{17}\) cm\textsuperscript{-3}, is achieved by using small TMGa exposure and large TBAs exposure.

**Conclusions**

GaAs growth by VALE has been studied under various growth parameters. The distinct self-limiting of the growth rate indicates the gas phase decomposition of TMGa is suppressed successfully in VALE. The unique gas handling system enhances the utilization of the source materials significantly. TBAs is a promising As source material in VALE. The carbon incorporation is a serious problem in VALE and the mechanism needs more investigation. Low carbon films can be grown by decreasing the TMGa exposure and increasing the TBAs exposure. The major task for the future applications of VALE will be the reduction of the carbon incorporation at high growth rates.
References


Figure 1 - Dependence of the growth rate for VALE of GaAs as a function of TMGa exposure time and exposure level.
Figure 2 – Dependence of growth rate for VALE of GaAs as a function of temperature showing a 80° - 100°C range of temperatures over which self-limiting growth is observed.

Figure 3 – Dependence of the measured carrier concentration in VALE – grown GaAs films as a function of TBAs exposure.
The major objectives of this research were to (1) use a wide range of spectroscopic techniques to compare the optical properties of homogeneous, disordered Ga$_{0.52}$In$_{0.48}$P (GaInP) to the more unusual ones observed in inhomogeneous ordered material; (2) correlate those optical properties to details of the microstructure in an attempt to understand how the microstructure is responsible for the unusual optical properties; (3) investigate the fundamental processes involved in the modulation of photoluminescence (PL) by a microwave electric field and develop the technique into a mature technology.

Approaches

Optical investigations of GaInP utilized conventional, selectively excited, time resolved and microwave modulated PL (MMPL) and resonant Raman spectroscopy in close cooperation with collaborators at NREL both growing samples and characterizing them via reflectance difference spectroscopy and transmission electron microscopy (TEM). Because of anticipated similarities between ordered GaInP and intentionally disordered AlAs/GaAs superlattices (d-SL), extensive comparisons of the optical properties of these two systems were performed.

Research Results

The low temperature band gap of "perfectly disordered Ga$_{0.52}$In$_{0.48}$P", the composition lattice-matched to GaAs substrates, was determined by the procedure illustrated in Fig. 1 to be 2.015 ± 0.007 eV, calculated to be 8.5 meV larger than the measured free excitonic absorption energy and in agreement with published results from one other group. The band gap of ordered GaInP is not well defined. In fact it was determined in this work that the band gap of ordered GaInP is not even well defined for a single sample! To date there has been an uncertainty of as much as 30 meV among published data. The number is important for two reasons. Many researchers use band gap reduction as an indication of "degree of ordering"; hence a standard for "no ordering" is required. Additionally, Wei et al. predict that all ordering-dependent material properties vary as the square of the long-range order parameter. One such property is the ordering-induced splitting of the valence band, which we have measured as a function of band gap reduction. The experiments producing some of the samples used in this study have also shown that disordering via P$_4$-annealing proceeds from the free surface of the epilayer toward the interface rather than nucleating homogeneously throughout the layer.

The combination of PL, PL excitation (PLE) and time resolved PL allowed us to determine that the dominant radiative recombination process seen in weakly ordered MBE-grown and
all disordered (LPE-grown or P₄-annealed) GaInP samples is excitonic⁶ while, with a few exceptions, the dominant processes seen in ordered materials are most definitely not excitonic. Furthermore, in the weakly ordered samples showing bound (localized) excitonic emission, the localization energy was found to vary by as much as a factor of four.

A very strong tailing of states below the "band edge" was observed in many ordered materials, particularly those containing small domains of both ordering variants. This tailing is "strong" in terms of both the density of states into which light can be absorbed and the energy range over which the absorption occurs. The presence of band tail states and emission processes with excitation intensity dependent lifetimes and energies appears to correlate with boundaries between domains ordered in different variants rather than with the existence of ordering per se. (All these effects are very weak in samples with large domains and a single variant of ordering.)

Microwave modulated PL spectra of ordered GaInP often show a negative peak associated with higher energy processes, a positive peak at lower energy. As shown in Fig. 2, this is exactly the opposite of what is normally observed in homogeneous materials where radiative recombination involves shallow bound states which are energy minima. In ordered GaInP, the carriers whose energies are increased by the microwave electric field preferentially contribute to processes at lower energy. This in turn means that the states at higher energy were metastable. All of this is compatible with a model in which the epilayer consists of an ensemble of domains having different degrees of ordering and hence different band gaps.

Because of similarities in band structures, optical comparisons were made between ordered GaInP and intentionally disordered AlAs/GaAs superlattices. A number of previously reported observations of general properties of the disordered superlattices were repeated, confirming the generality of material properties previously reported by only one group. Different disordering schemes were also added.⁸⁻⁹ Time resolved PL measurements at 50 K show a stretched exponential decay of the luminescence. This observation gives the first definitive confirmation that disorder-induced carrier localization is dominating the optical properties. A new d-SL structure with less stringent constraints on layer thickness was found to have properties intermediate between the d-SL's with narrower constraints and true multiple single quantum wells (MSQW): although the density of tail states increases in this structure, the PL has only a very weak dependence on temperature or excitation intensity, traits generally characteristic of MSQW's and very different from the dependences for the SL's previously studied.

A comprehensive study of the fundamental characteristics of MMPL, including both experiments and numerical modelling, showed that both impact ionization and the energy dependences of the capture cross-sections of competing radiative and non-radiative processes are important in mediating the microwave-PL interaction.¹⁰

Conclusions

As a result of the past year's work, we are able to report that: (1) the low temperature band gap of "perfectly disordered Ga₀.₅₂In₀.₄₈P" is 2.015 ± 0.007 eV, a result of both theoretical
and experimental significance. Hence we can with certainty report that many samples grown by OMVPE and MBE and heretofore routinely referred to as "disordered" in fact contain measurable amounts of ordering. (2) In weakly ordered GaInP the excitons are localized at band edge fluctuations rather than the impurity localization which characterizes homogenous materials. (3) Because the Stokes shift between the absorption edge observed in PLE and the nearest emission (i.e. PL) varied between as little as 3.3 meV and more than 30 meV, we were able to establish that, although commonly used in the literature, PL emission energy is a poor measure of band gap, particularly when ordered and disordered samples are being compared. (4) The presence of band tail states and emission processes with excitation intensity dependent lifetimes and energies appears to correlate with boundaries between domains ordered in different variants rather than with the existence of ordering per se. (5) MMPL suggests that the dominant radiative recombination processes at low temperatures in strongly ordered 2-variant GaInP involve local (metastable), rather than global, equilibrium states.

With respect to the comparison between the properties of ordered GaInP and disordered AlAs/GaAs superlattices, we have learned that there are some similarities and some differences. The disordered AlAs/GaAs superlattice and ordered 2-variant GaInP both definitely show a reduction in band gap and, in nearly all cases for GaInP, a high density and broad extent of tail states. Both systems show increased radiative lifetimes but lack a single time constant. The disordered superlattices do not, however, show either the excitation-intensity dependent emission energy or lifetime common in ordered (particularly 2-variant) GaInP.

Future work will focus on continuing to advance our understanding of how details of the microstructure of partially ordered GaInP determine its unusual optical properties and on extending our investigations to other ordered ternary compounds as well as direct investigation of the solar cells of which ordered GaInP forms a crucial component.

References

1. The Band Gap of "Perfectly Disordered" Ga_{0.52}In_{0.48}P, M. C. DeLong, D. J. Mowbray, R. A. Hogg, M. S. Skolnick, J. E. Williams, Sarah R. Kurtz, J. M. Olson, M. C. Wu and M. Hopkinson), to be published in AIP Conference Proceedings (1994).


Figure 1 Free exciton absorption energy (PLE) as a function of lattice mismatch (i.e. composition).

Figure 2 PL (dashed) and MMP (solid) from a GaAs homostructure (left) and GaInP/AlInP double heterostructure (right).
3.0 POLYCRYSTALLINE THIN FILMS PROJECT

Ken Zweibel, (Manager)

Polycrystalline thin films made from CuInSe$_2$ (CIS), CdTe, and film silicon continued to make strong progress during FY93. Numerous performance records were achieved, indicating ongoing strong interest in the field as well as the substantial opportunity for continued improvements. Cadmium telluride-based module efficiencies at key companies began to approach levels considered reasonable for commercialization: i.e., 'champion' modules reached nearly 8% (Table 1) in large areas (3000 to 7000 cm$^2$) and yields of good modules (above 7%) began to be attractive. Indeed, both US CdTe companies 'graduated' to PVMat contract winners during the year, indicating the strong evolution of these DOE/NREL-partnered successes. In CIS, we began to emerge from the 'shadow' of having only one serious US CIS company (Siemens Solar Industries) as ISET and EPV made their first 5%-7% one square foot submodules. Still, the CIS field remains relatively dominated by SSI, and thus vulnerable to its corporate 'upsets'. However, during this period SSI re-established itself as a serious CIS company by raising the yield on its experimental devices by about 2% (absolute) to almost 13% efficiency. As they translate this into larger area prototypes, we should see renewed vigor (perhaps in 1994) in CIS module efficiencies. We have some chance thereby of achieving our stated Five Year Plan goals for thin films of 11% and 12% for power modules (4000 cm$^2$ or larger). No other thin film (e.g., CdTe, film silicon) has a chance of meeting these goals in the next year or two.

Table 1. The Best Polycrystalline Thin Film Modules (1993)

<table>
<thead>
<tr>
<th>Material</th>
<th>Size (cm$^2$)</th>
<th>Efficiency (%)</th>
<th>Power (Watts)</th>
<th>Company &amp; comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>6879</td>
<td>7.7%</td>
<td>53.1 W</td>
<td>Solar Cells Inc.</td>
</tr>
<tr>
<td>CuInSe$_2$ (CIS)</td>
<td>3883</td>
<td>9.7%</td>
<td>37.8 W</td>
<td>Siemens Solar Industries</td>
</tr>
<tr>
<td>CdTe</td>
<td>3528</td>
<td>7.7%</td>
<td>27.5 W</td>
<td>Golden Photon Inc.</td>
</tr>
<tr>
<td>CuInSe$_2$ (CIS)</td>
<td>938</td>
<td>11.1%</td>
<td>10.4 W</td>
<td>ARCO Solar (now Siemens Solar Industries)</td>
</tr>
<tr>
<td>CdTe</td>
<td>1200</td>
<td>8.7% (reported)</td>
<td>10.0 W</td>
<td>Matsushita (Japan)</td>
</tr>
<tr>
<td>CdTe</td>
<td>706</td>
<td>10.0%</td>
<td>7.1 W</td>
<td>BP Solar (Great Britain)</td>
</tr>
<tr>
<td>CIS</td>
<td>845</td>
<td>5.8%</td>
<td>6.9 W</td>
<td>ISET</td>
</tr>
</tbody>
</table>

Note: Efficiencies verified independently at NREL unless noted as 'reported'.

Good news continues in terms of the 'pipeline' of future results. Some of the most outstanding progress occurred in the applied R&D portion of the program, in which several groups made
record efficiency laboratory cells. Table 2 shows the best cells made during the year, highlighted by NREL-made CIS cells that set the record for this material (and any thin film) at 15.9%. Along with CdTe at 15.8%, this indicates that there are major, future opportunities for polycrystalline thin film modules to advance beyond the current state of the art. Indeed, it seems that our long-stated goal of 15% thin film modules now appears likely to be achieved. In the past, we had little support for the idea that thin films could be this efficient. Cell results in CIS and CdTe have changed that paradigm (see also Figure 1, the record cell efficiencies by year).

Table 2. Record Laboratory Cells Made in FY93 (date of NREL verification)

<table>
<thead>
<tr>
<th></th>
<th>Date</th>
<th>Material</th>
<th>Efficiency</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>NREL</td>
<td>10/7/93</td>
<td>CIGS/CdS/ZnO</td>
<td>15.9%</td>
<td>0.44 cm²</td>
</tr>
<tr>
<td>NREL</td>
<td>8/27/93</td>
<td>CIGS/CdS/ZnO</td>
<td>13.9%</td>
<td>6.6 cm²</td>
</tr>
<tr>
<td>EuroCIS</td>
<td>7/93</td>
<td>CIGS/CdS/ZnO</td>
<td>14.8%</td>
<td>0.38 cm²</td>
</tr>
<tr>
<td>Boeing</td>
<td>8/25/93</td>
<td>CIGS/CdS/ZnO</td>
<td>14.6%</td>
<td>0.995 cm²</td>
</tr>
<tr>
<td>U. S. Florida</td>
<td>11/19/92</td>
<td>CdTe/CdS/SnO₂</td>
<td>15.8%</td>
<td>1.08 cm²</td>
</tr>
</tbody>
</table>

During 1993, in-house NREL assumed a leadership role in CIS R&D. This role is symbolized by the achievement of world record cell efficiencies (e.g., those in Table 2 and Figure 1). However, more importantly, these cells were made by a new deposition method designed by NREL to possibly relieve some of the manufacturing-related issues associated with CIS. As a result, we are working in close collaboration with the entire US CIS industry (Siemens Solar, Energy PV, ISET, Martin Marietta, Solarex) to explore how our new knowledge can help them to accelerate the CIS technology. In at least three cases, we are exploring potential non-exclusive licensing agreements. The knowledge gained by our growing insights into how device-quality CIS forms (independent of any deposition method) is building a good foundation for a renewed attack on manufacturing-related issues such as areal uniformity, yield, machine design and tolerance, and adhesion.

During FY94 we will be re-competing our industrial subcontracts program in polycrystalline thin films. The RFP will be mailed in early 1994, with proposals due in the spring. New three-year cost-shared subcontracts will be awarded at the beginning of FY95. The purpose of the RFP will be to continue the development of the prototype module technologies reviewed in this annual report. Specifically, we will be addressing module efficiency issues, module design, and prototype processing issues. Continued success in these areas should assure ongoing momentum for these important thin film PV options.
Polycrystalline Thin Film PV Efficiencies
Best Laboratory Cells

- CuInSe2
- CdTe

U. South Florida
BP Solar
U. S. Florida
NREL
Euro CIS
Boeing
CIS
Photon Energy

ARCO
Kodak
Boeing
AMETEK
Boeing

Matsushita
Monosolar
Kodak
Boeing
U. Maine

Boeing
Boeing

5% 7% 9% 11% 13% 15% 17%

Standard conditions
Deposition of CdTe Thin Films and Solar Cells

National Renewable Energy Laboratory

T. J. Coutts, Group Leader and Principal Scientist
K. Ramanathan, Senior Scientist
T. A. Gessert, Staff Scientist
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Objectives

• Identify and develop device structures and deposition processes capable of producing efficient CdTe PV devices.

• Develop an alternate CdTe/metal contact system which is both stable and manufacturable.

Technical Approach

In FY93, the CdTe effort has concentrated on two promising deposition techniques. The first of these is close spaced sublimation (CSS), which has produced the best devices and is similar to a process used by industry for large scale depositions (Solar Cells, Incorporated). The second technique, sputter deposition, may provide an alternative to CSS for large-area in-line production requirements. In addition, we have studied alternate CdTe/metal contact systems. Discussions with industry reveal that development of a stable, reproducible, and manufacturable ohmic back contact to p-type CdTe is of paramount importance. Therefore, a program investigating alternatives to the commonly used graphite-based contact has continued. A summary of the results in these areas are outlined below.

Results

CSS CdTe Deposition and Devices:

Soda lime substrates were used as starting material for CdS/CdTe solar cell fabrication. Although the best devices have been produced on borosilicate glass, soda lime glass is the substrate of choice for industrial production of CdTe modules (due to its lower cost). The challenge is to modify the CSS deposition parameters and processing conditions, developed for borosilicate glass, to accommodate soda lime glass substrates and the resulting material. The lower substrate temperatures, required for soda lime glass, affect both the CdTe grain size and the film morphology. Soda lime glass substrates were provided by Watkins-Johnson and Libbey Owens Ford (LOF) and were coated, by the manufacturer, with specular SnO2 (sheet resistance of 10 Ω/square). We have developed a CdS solution growth process for depositing thin high-quality layers on substrates up to 100 cm². These CdS/SnO2 coated soda lime substrates were used for CSS CdTe depositions. For soda lime glass, substrate temperatures between 500-600°C.
were explored and post deposition CdCl₂ heat treatment procedures were established. We find that CdCl₂ treatments do not affect the CdTe grain size, but do significantly improve the minority carrier lifetime. Although not fully optimized, these efforts resulted in a 10.6% efficient device on soda lime glass and a 10.9% efficient device on borosilicate glass. In separate cells on soda lime glass, open circuit voltages as high as 840 mV have been measured.

The above results were obtained using a simple CSS reactor obtained from the University of South Florida. An effort was initiated to develop a more sophisticated CSS reactor for future research. We have completed the initial design phase for this CSS reactor. The new reactor will feature several enhancements not found on the present CSS system. These include:

- Fully automated process control system for improved repeatability and temperature profiling.
- Fully automated and modular gas introduction system.
- Improved source and substrate temperature uniformity over a 2" x 2" area.
- Clean sample introduction/preparation work area.
- Extensive safety features and interlocks.

Final design and construction of this deposition system will be completed in FY94 in the SERF laboratory.

*Sputter Deposited CdTe Materials and Devices:*

CdTe thin films were deposited by rf-magnetron sputtering over a wide range of conditions. Structural variations were assessed using X-ray diffraction, SEM, and a technique developed in-house to measure residual stress. Results indicate that the microstructure and stress of the films are sensitive to the deposition conditions and annealing procedures. Specifically, films deposited at room temperature are columnar, demonstrating a mixture of cubic and hexagonal phases. These films form with the preferential column axis along the cubic [111] direction. In contrast, films deposited at elevated substrate temperatures (~400°C) consist of a closely packed array of cubic-phase polycrystalline grains. The CdCl₂/annealing treatment reorganizes the CdTe microstructure from a columnar to a granular structure, and changes the preferred orientation. The treatment also tends to reduce the residual stress that accumulates during film formation, and thereby improves the crystallinity of the grain. Following the CdCl₂ treatment, the CdTe films exhibited enhanced light and dark conductivity and an increased optical band gap.

Using the optimized conditions obtained in the above study, CdS/CdTe devices were fabricated. rf-sputtered CdTe layers were deposited on both evaporated and solution grown CdS layers on a SnO₂/LOF glass substrates. Back contacts consisted of evaporated Cu/Au bi-layers with thicknesses of 20 Å and 1000 Å, respectively. The best devices had the following characteristics: $V_{oc} = 802 \text{ mV}$, $J_{sc} = 19.74 \text{ mA/cm}^2$, $FF = 67.77 \%$, and $\eta = 8.2 \%$. In general, these devices had short circuit currents and fill factors that were inferior to state-of-the-art CdTe devices made by the CSS process.

*CdTe Back Contact Studies:*

Device studies in early FY93 demonstrated that sputtered deposited CdTe was of adequate quality for device applications. Therefore, this material was used for contact studies to
investigate the effects of various contact schemes on device parameters. Results from these investigations led to the following conclusions: i) The amount of CuCl₂ in the graphite-paste contact greatly affects the amount of extrinsic doping observed in CdTe/CdS devices (it appears that the graphite-paste is not very effective at limiting Cu diffusion into the CdTe); ii) The procedures required to apply the graphite-paste contact, make it difficult to obtain reproducible contact sizes and interfacial characteristics; iii) When Cu is used in a Cu/Au-type contact, the thickness of Cu must be limited to less than 100 Å or contact shorting will result; iv) Contacts formed with 0.7% Cu-doped ZnTe and Ni (annealed at 200°C) produce device characteristics similar to a devices made with graphite-paste contacts incorporating very low levels of CuCl₂ (i.e., very little evidence of extrinsic Cu doping of the CdTe). Combined with the above results, this observation suggests that the ZnTe may be better at limiting Cu diffusion into the CdTe than the graphite paste. If true, and if Cu diffusion to the junction is a mechanism of degradation in a CdTe/CdS device, this would imply that the Cu-doped ZnTe contact may provide a much more stable contact than CuCl₂-doped graphite paste.

With the above preliminary results in mind, the contact studies proceeded in two principle directions: i) Identifying processes that could be used to fabricate contact-resistance patterns of Ni on CdTe, Ni on Cu-doped ZnTe, and Cu-doped ZnTe on CdTe (these processes are necessary to quantify contact resistance at these critical interfaces). ii) Studying the effect of deposition conditions on material parameters of undoped and Cu-doped, rf-sputtered ZnTe. Preliminary results indicate that using the Cu-doped ZnTe interfacial layer reduces the measured contact resistance by more than an order of magnitude compared to a Ni/CdTe contact produced by a similar process. These investigations have resulted in numerous observations, most confirming speculation that Cu-doped ZnTe is a promising interfacial layer for a CdTe contact. These, and other observations, are presented in two papers that were prepared and presented in FY93.4,5

Future Directions

Due to limited resources, in FY94, the task will focus on CSS deposited CdTe (work on sputter deposited CdTe material will be suspended). The emphasis will be towards developing optimized processing sequences for improved device performance and developing a fundamental understanding of what is happening at the critical CdS/CdTe interface in CSS material. We will continue our work on developing a high-performance, manufacturable ohmic contact with a demonstration of the Ni/ZnTe:Cu/CdTe contact system. the program will also concentrate on building the infrastructure necessary to produce a complete CdS/CdTe device structure at NREL. This will include developing the capability to deposit high-quality transparent conducting oxides and barrier layers as well as completing a state-of-the-art CSS deposition system.

Publications/Presentations


Development of Polycrystalline Thin Film Devices Based on Cu(In,Ga)Se₂

Contributors:

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A. Tennant, Associate Staff Scientist
J. Dolan, Master Technician
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A. Gabor, Graduate Student, CU
Y. Qu, Graduate Student, CSM
D. Du, Graduate Student, CSM

Objectives

• Enhance the technology base of CIS PV by understanding and improving the materials, processes, and cell structures to achieve high efficiency conversion.
• Assist industry to develop deposition processes, cells, and prototype module technologies.

Technical Approach

(1) Improve the performance of devices (efficiency) by enhancing the quality of the materials and exploring new device structures.
(2) Arrive at a universal growth model for Cu(In,Ga) (Se,S)₂ (CIGSS) polycrystalline thin-films which is process independent. This will insure the reproducibility of the device quality CIGSS.
(3) Develop road maps for the various reaction pathways which will yield device quality CIGSS, which can be adapted to manufacturing processes. The road map should point out issues relevant to manufacturing.
(4) Work with industry on technical transfer. Optimally, industry work towards replicating what we have done, while we work towards reproducing our results under their constraints.

Results

Device Development We have fabricated high efficiency Cu(In,Ga)Se₂ (CIGS) based PV devices by four different methods. A world record total area efficiency of 15.9% has been achieved with a simple CIGS fabrication process. A growth model has been developed to describe the film growth dynamics. The four processes used to fabricate the high efficiency devices are summarized in Table I, with a description of the possible chemical reaction path leading to the compound, and the process issues that are attractive for manufacturing.

Within the four processes we investigated, three absorber structures: (1) homogeneous CIS (E_g=1.0 eV), (2) homogeneous CuIn₀.₇₅Ga₀.₂₅Se₂ (E_g=1.18 eV) and (3) graded Cu(In,Ga)Se₂ (E_g=1.0-1.7 eV). In figure 1, the light I-V results are presented for devices fabricated by the above described processes. The total area efficiencies range from 12.6 to 15.9%. The latter represents a NREL confirmed world record for all non-single crystalline thin-film technologies.

Absorber Fabrication In Figure 2, we summarize graphically in the form of a growth model, the formation dynamics of the thin-film absorber. It first involves the accommodation/condensation of elemental Cu and In onto the heated substrate. For temperatures above ~150°C, in vacuum, elemental Se will not condense on the substrate surface. Instead, the Se vapor will accommodate through reactions with the metals on the surface to form CuₓSe and InₓSe binaries (Fig. 2a). The former reaction rate dominates and the formation of the CuₓSe:CuInSe₂ mixture progresses according to Eqs. (1)-(3).
For $T_{\text{sub}} \geq 500^\circ \text{C}$,

$$x\text{Cu}(s) + \frac{1}{y}\text{Se}_y(g) \rightarrow \text{Cu}_x\text{Se}_{(s,l)}, (1 \leq x \leq 2) \quad (1)$$

For $T_{\text{sub}} \geq 500^\circ \text{C}$,

$$\text{Cu}_x\text{Se}_{(s,l)} + (x-1)\text{Se}_y(g) \rightarrow x\text{CuSe}(l) \quad (2)$$

$$y\text{CuSe}(l) + \text{In}(l) + \text{Se}_y(g) \rightarrow \text{CuInSe}_2(s) + (y-1)\text{CuSe}(l) \quad (3)$$

For substrate temperatures greater than $500^\circ \text{C}$, the process is influenced by the co-existence of a solid and liquid phase (Fig. 2b). The phase separation occurs lateral to the growth plane. As sufficient material is added to the substrate, the $\text{Cu}_x\text{Se}(l)$ and $\text{CuInSe}_2(s)$ regions coalesce (Fig. 2c). The liquid-phase enhances adatom surface mobility and facilitates mass transport of the binary and ternary products. For smooth, amorphous surfaces with low nucleation-site densities (e.g. Corning glass), the formation of $\text{CuInSe}_2$ surfaces parallel to the $<111>/<112>$ lattice planes is preferred. This usually allows films to evolve with exclusive (112) orientation. On other surfaces, such as a 1.0µm layer of Mo deposited on SLS, films typically evolve with preferred (112). As the $\text{CuInSe}_2$ solid coalesces, the surface tension between the liquid and solid phases increases and reaches a critical value, at which time the phase separation converts to an orientation normal to the growth plane (Fig. 2c). The result is a layered structure with a predominance of the $\text{Cu}_x\text{Se}$ at the surface.

In the second stage of the growth process, the $\text{Cu}_x\text{Se}$ is alleviated by the chemical conversion to $\text{CuInSe}_2$ (Fig. 2d). The reaction is described in Eqs. (6) and (7)

$$\text{In}(\text{vapor}) \rightarrow \text{In}(l) \quad (4)$$

$$\text{Cu}_x\text{Se}(l) + \text{In}(l) + \text{Se}_y(g) \rightarrow \text{CuInSe}_2(s) \quad (5)$$

Historically, this stage of the process involved an In-rich/Cu-deficient vapor flux. The arguments here propose that Cu is not required during the conversion process. If Cu is present in this stage, the mass balance is modified only by the addition of $\text{Cu}_x\text{Se}$ to the pool. The exclusion of Cu from the final stages of film formation will facilitate the application of the process to a manufacturing environment.

Fig. 1  I-V measurements of Cu(In,Ga)Se$_2$-based device structures. (VIC = Vapor-Induced Conversion)

$$x\text{Cu}(s) + \frac{1}{y}\text{Se}_y(g) \rightarrow \text{Cu}_x\text{Se}_{(s,l)}, (1 \leq x \leq 2) \quad (1)$$

$$\text{Cu}_x\text{Se}_{(s,l)} + (x-1)\text{Se}_y(g) \rightarrow x\text{CuSe}(l) \quad (2)$$

$$y\text{CuSe}(l) + \text{In}(l) + \text{Se}_y(g) \rightarrow \text{CuInSe}_2(s) + (y-1)\text{CuSe}(l) \quad (3)$$
Table 1. Description of absorber processes utilized to fabricate Cu(In,Ga)Se2 absorbers

<table>
<thead>
<tr>
<th>Pictorial Description</th>
<th>Chemical Reaction Path</th>
<th>Manufacturing Issues</th>
</tr>
</thead>
</table>
| Start \(\rightarrow\) Finish                                                            | \((\text{In, Ga})\text{Se}_x + \text{Cu}_x\text{Se} + \text{Se} \rightarrow 550^\circ \text{C} \text{Cu(In,Ga)}\text{Se}_2\) | • Separates Cu & (In, Ga) delivery
  • Simplifies in-situ process control
  • Conducive to large-area deposition technology |
| (a) Vapor Induced Conversion of an (In, Ga)-rich Precursor (2-stage)                     |                                                                                        |                                                                                      |
| \(\text{Cu}_x\text{Se} \rightarrow \text{graded Cu(In,Ga)}\text{Se}_2\)                |                                                                                        |                                                                                      |
| (b) In-line / Variable Flux Process (1-stage)                                           | \(\text{Cu} + (\text{In, Ga}) + \text{Se} \rightarrow 500^\circ \text{C} \text{Cu(In,Ga)}\text{Se}_2 + \text{Cu}_x\text{Se}\) | • Designed for in-line, continuous, large-area deposition
  • Process design flexibility                                                                 |
| Variable (Cu, In, Ga, Se) Flux \(\rightarrow\) Graded Cu(In,Ga)Se2                     | \(\text{Cu} + (\text{In, Ga}) + \text{Se} + \text{Cu}_x\text{Se} \rightarrow 550^\circ \text{C} \text{Cu(In,Ga)}\text{Se}_2\) |                                                                                      |
| (c) Vapor-Induced Conversion of a Cu-rich Precursor (2-stage)                           |                                                                                        | • Stage 1 Cu-rich precursor can be easily synthesized
  • Stage 2 conversion does not require Cu                                                                 |
| \(\text{CuCl}_{\text{In} \rightarrow \text{Cu}_x\text{Se}} \rightarrow \text{Graded Cu(In,Ga)Se}_2\) |                                                                                        |                                                                                      |
| (d) Selenization of Mixed Metallic Precursors (2-3 stages)                               | \(\text{Cu} + \text{In} \rightarrow \text{Cu}_{11}\text{In}_9 + \text{In}\)              | • Separates deposition processes from thermal/chemical processes
  • Utilizes established large-area metal deposition technology                            |
| \(\text{Cu}_x\text{Ga} + \text{Se(g)} \rightarrow \text{graded Cu(In,Ga)}\text{Se}_2\)    | \(\text{Cu}_{11}\text{In}_9 + \text{In} + \text{Se} \rightarrow 300^\circ \text{C} \text{Cu}_{11}\text{In}_9 + \text{Cu}_x\text{Se} + \text{In}_y\text{Se}\) |                                                                                      |
|                                                                                        | \(\rightarrow 450^\circ \text{C} \text{CuInSe}_2\)                                   |                                                                                      |

The relative orientation of the liquid and solid phases facilitates the diffusion/transport kinetics required for the conversion of the \(\text{Cu}_x\text{Se}\) into \(\text{CuInSe}_2\). As Fig. 2d depicts, the \(\text{CuInSe}_2\) is formed and transported in solution to the liquid-solid interface where epitaxial growth continues. As the conversion process nears completion, the surface coverage of liquid \(\text{Cu}_x\text{Se}\) is incomplete, and solid regions with a surface composition of \(\text{CuIn}_3\text{Se}_5\) will appear. In order to minimize the incorporation of excess In into the solid bulk regions (in contrast to the liquid \(\text{Cu}_x\text{Se}\) regions where the reaction chemistry described above will still hold), the Se/In vapor ratio is lowered to encourage the formation and subsequent volatilization of Se-poor In-Se compounds and discourage the formation of stable In-Se phases that may diffuse into the bulk and drive the composition Cu-poor. In this way, the process is self-limiting and stabilizes to a uniform \(\text{CuInSe}_2/\text{CuIn}_3\text{Se}_5\) bulk/surface composition. The change in surface chemistry is also conducive to an end-point detection scheme that either observes a transition in surface composition or state (liquid \(\rightarrow\) solid).

**Conclusion**

We have demonstrated the fabrication of high efficiency CIS-based devices by different methods designed to point out a universal approach to the growth of the thin-film absorber, which is
process independent. This technical approach allows us to set up road maps by which manufacturing processes can be developed for large scale production. In FY94, we expect to demonstrate enhanced efficiency of the CIS-based solar cell, in excess of 17%. We hope to validate the manufacturability of the process(es) which give high efficiencies, by fabricating and demonstrating large-area devices. This will be accomplished in two ways: (1) Large area devices will be fabricated entirely in-house to validate the different processing steps; (2) Large area devices (~100cm²) will be fabricated in collaboration with industry where the device/module will undergo the actual processing steps practiced by industry. With this exercise, we hope to demonstrate a large-area solar cell efficiency with 90% of that of the small device. On continuous basis during FY94, we intend to validate our processes and transfer the knowledge to industry.

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Fig. 2 Pictorial representation of thin-film CuInSe₂ growth model
Objective

The objective of this program is to develop Silicon-Film™ Product III into a low cost, stable solar cell for large scale terrestrial power applications. The Product III structure is a thin (<100 µm) polycrystalline layer of silicon on a durable, insulating, ceramic substrate. The insulating substrate allows the silicon layer to be isolated and metallized to form a monolithically interconnected array of solar cells. High efficiency is possible with the use of light trapping and surface passivation. The long term goal for the project is a 1200 cm², 18% efficient monolithic array. The objectives during this phase of the program were improving material quality (specifically minority carrier lifetime in the base layer) and demonstrating the feasibility of fabricating 100 cm² monolithically interconnected solar cell array devices on insulating ceramic substrates.

Background and Technical Approach

The Phase II effort of this program concluded that impurities originating from the low-cost ceramic were primarily responsible for the degradation of minority carrier diffusion length in the base layer of the solar cell devices [1]. Inductively coupled plasma - mass spectroscopy (ICP-MS) found a strong correlation between impurities found in the silicon layers and those found in the ceramic (tungsten, aluminum, copper, and chromium). Also, the minority carrier diffusion length of this material was not responsive to process enhancements (such as diffusion gettering or hydrogenation). Control material known to be free of impurities responded well. Furthermore, studies of crystallographic defects, such as grain boundaries and dislocations were not found to have any significant correlation to the quality of the material. Therefore, a focused effort was made during the Phase III program to develop a metallurgical barrier formation process that would limit the impurity interaction between the Silicon-Film™ layer and the ceramic substrate.

Results -- Metallurgical Barrier and Material Quality

Material quality has been the key issue in the development of Product III over the past year. Thin, large-grain polysilicon layers can be routinely grown on ceramic substrates using the Silicon-Film™ process, however, minority carrier diffusion lengths (L_n) had been limited to less than 10 µm. To address the contamination from the ceramic, several metallurgical barrier coatings for use between the ceramic substrate and the grown film were investigated.

The key properties of a good metallurgical barrier layer include wettability and survivability, effectiveness as an impurity diffusion barrier, conductivity, reflectivity (or transparency) and effectiveness as a back surface passivation layer. One of the difficulties in selecting a barrier material is finding one that allows wetting during the growth process. Dielectric materials, which
consist primarily of metal oxides and nitrides, are typically difficult to wet with molten metals. Although we have had some success with these materials, the dielectric barrier is not reproducible and depends on variables such as particle size and surface texturing.

Figure 1. Cross section of a silicon-ceramic interface: (a) no barrier present, and (b) with conformal barrier (note clear delineation between the two regions).

Recent efforts have revealed a new metallurgical barrier technology that exhibits many of the properties missing in the powder-based layer. Cross-section photomicrographs of silicon-ceramic interfaces separated by this barrier layer are shown in Figure 1. Figure 1(a) shows the silicon-ceramic interface for a structure formed without a barrier layer. Note that a high level of interaction between the ceramic and silicon has taken place. Figure 1(b) shows a similar silicon-ceramic interface with a barrier layer present. Note the clear delineation between the silicon film region and the porous ceramic. With a related structure we have achieved a high diffusion length of 45 µm and can routinely fabricate devices with diffusion lengths over 35 µm. This represents a significant improvement over the 5 - 8 µm diffusion lengths achieved without a barrier present (see Figure 2).

We have investigated a number of barrier layer deposition techniques. All new barrier types exhibit excellent wetting properties which allow uniformly thin (<100 µm) silicon films to be grown. The new barriers also exhibit low solubility in silicon and good survivability in the Silicon-Film™ process. Figure 3 shows cross-sectional photomicrographs of two distinctly different barrier structures (deposited by two different techniques) which have been deposited on single crystal silicon substrates.
Figure 2. *Quantum efficiency curves of devices fabricated from material grown with and without a metallurgical barrier layer.*

Figure 3. *Barrier structures deposited on single-crystal silicon substrates.*

Results -- Device Design and Fabrication

Critical issues for the development of the Product III device include electrical and mechanical requirements of the insulating ceramic, interconnection metallization spacing, element sizing, development of low-cost processing techniques and Silicon Film™ material quality.

The device processing sequence and the device modeling used to determine the spacing of isolation trenches and grid lines are described elsewhere [2][3]. To demonstrate the feasibility of
the process, complete integrated arrays have been fabricated on ceramic substrates. Early devices were shunted due to high ceramic conduction and metallization shunts, however, both problems have been solved and shunt conductances of less than 0.1 mS/cm$^2$ have been measured. The I-V curve of a 7 element array is shown in Figure 4. The open circuit voltage of the device is 3.9 volts (561 mV per element). The short circuit current is 35.2 mA (20.5 mA/cm$^2$) with a device area of 12 cm$^2$. The fill factor is 0.63 (high series resistance) with an overall device efficiency of 7.3%.

![Figure 4. I-V Curve of a 7 element Silicon-Film™ on ceramic sub module.](image)

**Conclusions**

Recent barrier structures have resulted in a dramatic increase in the minority carrier diffusion length of the thin silicon layer from 5 - 7 µm to 45 µm. The suitability of a number of different barrier processes will be investigated during the Phase IV program. Further improvements in minority carrier diffusion length are expected with continued barrier development. The feasibility of the ceramic-based photovoltaic module has been demonstrated. A 7-element array was fabricated with an open circuit voltage of 3.9 volts. Improvements in device efficiency are expected with increased material quality.

**Acknowledgment**

The work was funded by DOE through the National Renewable Energy Laboratory.

**References**


Objectives

The overall objective of this subcontract is the demonstration of large area, thin film CuInSe$_2$ photovoltaic modules using methods applicable to safe, high yield, high throughput manufacturing. Specific goals include the fabrication of a 12% 1 cm$^2$ cell, a 7W 1 ft$^2$ module, and a 50W submodule.

Approach

EPV believes that an all-vacuum approach for material deposition is required in order to achieve the level of control of thickness, composition and microstructure necessary for uniform, high performance CIS to be obtained repeatably over large area substrates [1]. Good results have been obtained by the selenization of appropriately formed Cu-In precursor layers using a process developed and refined by EPV [1-3]. All processing (CIS, CdS, ZnO, patterning) has so far been conducted at the 1 ft$^2$ level. To effectively address the many problems that can attend the fabrication of modules (including loss of adhesion, excessive series resistance, shunting, and so on) we decided to systematically document and quantify each of these problems, and to explore in parallel different routes for their solution. We also clearly recognized the potential benefits of having the flexibility to incorporate into modules high quality alloys with bandgaps greater than that of CuInSe$_2$. An effort on CuIn(Se,S)$_2$ alloys was therefore initiated and is underway. Another line of research is directed towards sidestepping the Cd issue through the development of Cd-free junctions.

Results

A 12.5% total area efficiency was achieved for a 1 cm$^2$ (nominal) CIS cell. The $V_{oc}$ for this cell was 490mV. The improvement in CIS quality is largely attributed to optimization of the selenization process [3]. Our strategy has been to largely suppress the loss of indium during selenization, rather than starting with In-rich precursors and allowing In loss to achieve a more favorable Cu/In ratio. The optimization was conducted with much greater efficiency following the installation of an upgraded means of process control for the selenization step. Precise and reproducible ramps of both
substrate and selenium source temperatures are now routinely achieved through real time computer control. The I-V curve for a cell with improved CIS is shown in Figure 1.

Other results at the device level include a study of the effect of Cu/In ratio, the discovery of a positive light soaking effect in some devices, and measurements of device performance at low temperatures [3]. For devices with Cu/In ratios close to stoichiometry (only slightly Cu poor) a plateau in conversion efficiency was found, while further decrease in the Cu/In ratio led to a rapid decline in efficiency and a reduction of long wavelength response. A positive light soaking effect that tended to improve less efficient cells more than high efficiency cells was observed. The main result is an increase in fill factor. The rate of improvement was found to be bias dependent. Temperature dependent measurements were found to be particularly informative regarding CIS junction behavior. By reducing the dark current through operation near 170°K, cell efficiencies in excess of 18% were obtained.

Higher bandgap chalcopyrite semiconductors of the type CuIn(Se_{1-x}S_x)_2 have been produced by co-evaporation of selenium and sulfur onto Cu-In precursor layers. Solar cells have been prepared on CISS material having roughly equal atomic concentrations of all four elements with efficiencies of the order of 8%. The spectral responses of CIS and CISS cells are compared in Figure 2.

Cd-free CIS solar cells have been fabricated with efficiencies in the range 8.5%-10%. As promising as this is, the efficiency gap between these cells and CdS/CIS cells has yet to be closed.

Considerable efforts were expended in the evaluation of alternative schemes for monolithic integration. As a result of this focused attack, a new and reliable module technology has been developed. A key achievement of FY 93 was the attainment of an NREL-verified 8.04% aperture area efficiency for a 20 cell mini-module embodying this new technology (see Figure 3). The average open-circuit voltage per cell was 455mV. Computer calculations have been performed for module power output as a function of cell width, ZnO sheet resistance, interconnect dead width, and CIS diode parameters. This modeling has been employed for optimal module design and choice of ZnO thickness. Advances made in the area of adhesion enable 1ft² modules to be reliably processed with zero peeling. For a 720 cm² aperture area CIS module a power output of 4.5W was obtained, corresponding to an aperture area efficiency of 6.2%. The I-V curve for this module is shown in Figure 4.
Conclusions and Future Plans

A new module interconnect technology was developed in this phase, thereby allowing the achievement of significant advances in module efficiency. A key result was verification of an aperture area efficiency of 8.04% for a 20 cell mini-module. For a module approaching 1 ft² in size an aperture area efficiency of 6.2% was achieved. Continued optimization of the selenization process resulted in the achievement of a 12.5% 1 cm² cell efficiency. Cell and module results are summarized in Table 1.

In the next phase of this project we will focus on improvement of module efficiency, scale up of CIS deposition to 0.6 m², module encapsulation and outdoor testing, and further development of non-Cd and CISS devices.

Using CISS we hope to demonstrate the following benefits: a) superior efficiency of graded bandgap devices, b) use of wider cells in modules, thereby reducing area loss and reducing patterning time, c) reduced operating temperature sensitivity in modules (this has already been demonstrated for cells [3]). In the module area we will strive to achieve the already demonstrated 8% aperture area efficiency but on a 1 ft² module, thereby reaching the 7W goal. This will require careful analysis of loss factors in existing modules.

References


Table I. Parameters for CIS and CISS cells and modules

<table>
<thead>
<tr>
<th>Material</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA)</th>
<th>FF (%)</th>
<th>Area (cm²)</th>
<th>Efficiency (%)</th>
<th>Comments*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CISS</td>
<td>555mV</td>
<td>29.7</td>
<td>56.1</td>
<td>1.16</td>
<td>8.0 (act)</td>
<td>grid, no A/R, NREL</td>
</tr>
<tr>
<td>CIS</td>
<td>457mV</td>
<td>39.5</td>
<td>68.2</td>
<td>1.1</td>
<td>11.2 (act)</td>
<td>grid, A/R, NREL</td>
</tr>
<tr>
<td>CIS</td>
<td>490mV</td>
<td>37.7</td>
<td>67.6</td>
<td>1.0</td>
<td>12.5 (tot)</td>
<td>gridless, A/R, EPV</td>
</tr>
<tr>
<td>CIS</td>
<td>9.1</td>
<td>55.2</td>
<td>61.2</td>
<td>38.3</td>
<td>8.04 (ap)</td>
<td>20 cells, NREL</td>
</tr>
<tr>
<td>CIS</td>
<td>21.5</td>
<td>395.0</td>
<td>52.6</td>
<td>720.0</td>
<td>6.20 (ap)</td>
<td>52 cells, EPV</td>
</tr>
</tbody>
</table>

* Origin of PV electrical measurements (NREL or EPV) denoted in Table.
EPV CdS/CuInSe$_2$

Sample: #3  
Oct 12, 1993 1:24 PM  
Temperature = 25.0°C  
Area = 0.9785 cm$^2$  
Spectrum: ASTM E892-87 Global  
Irradiance: 1000.0 Wm$^{-2}$

Temperature: 25.0°C  
Area: 0.9785 cm$^2$

Fig. 1 Illuminated I-V curve for a gridless CIS cell with a total area efficiency of 11.8%.

Fig. 2 Spectral response of a Culn(Se,S)$_2$ cell compared to that of a CulnSe$_2$ cell.

EPV CIS Submodule

Sample: 8-30-1-3B  
Oct 7, 1993 11:57 AM  
Temperature = 25.0°C  
Area = 38.28 cm$^2$  
Spectrum: ASTM E892-87 Global  
Irradiance: 1000.0 Wm$^{-2}$

Fig. 3 Illuminated I-V curve for a 20 cell CIS module employing new interconnect technology (8% aperture area efficiency, 455mV per cell $V_{oc}$).

Fig. 4 I-V curve for a 6.2% 720cm$^2$ module.
Introduction and Objectives

In September of 1992, Golden Technology (GTC), a subsidiary of Adolph Coors Technology Company (ACX) of Golden, Colorado, purchased Photon Energy, Inc. (PEI) of El Paso, Texas with the objective of commercializing low-cost, high-performance photovoltaic modules. The new company name is Golden Photon, Inc. (GPI).

A 2 MW facility in Golden, Colorado, is under construction by GPI for proving the feasibility of the commercialization of photovoltaics. Process Prove-In in this new facility is expected to occur in the first half of 1994. Assuming that all the product qualifications are successfully passed during that period, product is expected to become commercially available by mid-1994.

The GPI objectives in Photovoltaics are covered through continuing advancement in three major areas; specifically, module efficiency, reliability and cost.

The specific objectives of this three phase program include:

• To achieve active area efficiencies of greater than 14% on small cells,
• To achieve aperture area efficiencies of greater than 13% on 1 ft² modules,
• To achieve aperture area efficiencies of greater than 12.5% on 4 ft² modules,
• To achieve greater than 20-year module life (based on life testing extrapolations) with no greater than 10% efficiency degradation.

Small Device Efficiency and 1ft² Modules

During the last year, much of the effort was re-focused onto 4 ft² module output improvement and encapsulation issues; however, several other notable milestones follow:

• A 12.7% device with an area of 0.302 cm² was measured at NREL with 12.7% efficiency.
• Open circuit voltages of 840mV to 846mV on small devices were measured at NREL.
• Short Circuit Currents of greater than 26mA/cm² on small devices were measured at NREL.
• The measurement irregularities defined in last year's annual report have been satisfactorily resolved.
• Aperture area efficiencies of over 8% were achieved on 1 square foot modules. (Average active area efficiencies near 10% were measured on the same modules.)

Four Square Foot Module Results

Significant improvement of 4ft² module output and design has been attained within the last year. Through identification and incorporation of improved deposition techniques, total
module layer uniformity improved significantly, resulting in notable improvements in overall module output as well as the distribution of module outputs within a batch. Figures 1A and 1B show an early and a more recent module output distribution to substantiate the improvements that have also been made in process control.

The historical trends shown in Figure 2 indicate that improvements in average module output were able to be made in a relatively consistent manner as the quality control program evolved. Confirmation of the continuing positive outcome of these efforts has been further validated at NREL by the performance tests of a set of 6 4ft² modules that were delivered to NREL for baselining and life testing. This set of six modules averaged 25.3 watts (normalized to a pyranometer reading in outdoor tests) with a 3% standard error for the distribution. The average aperture area efficiency of this batch measured 7.5%. The total area efficiency of the best module (26.5 watts) was 7.0%. The aperture area of the best module was 8.0%. The average active area efficiency of the best module was 9.1%. The rather poor utilization of the active/total area of the module is primarily due to the 12-14% optical loss caused by the poorly optimized interconnection methods that have been utilized. In spite of what remains to be accomplished, these confirmed module outputs achieve the initial internal product milestone for GPI.

A new design for encapsulation was adopted in late 1992. Qualification testing of the modules manufactured in El Paso appears successful. A number of design iterations have occurred and a great deal has been learned from the qualification testing done thus far. No significant problems are expected to be encountered during such qualification testing of the modules produced in the new 2MW facility.

Figure 3 shows the initial life testing results of the first generation of the improved encapsulation design. With this improved encapsulation design, the quality control issues during processing appear to be the only significant remaining issue with reliability. A number of these first generation modules broke in the field, but subsequent design improvements in the module seem to have resolved this issue. With over 175 days of exposure so far, the outdoor performance for the CdTe modules has remained within 5% of their initial baseline tests.

Environmental and Employee Health and Safety Issues

During Phase 2, a great deal of effort was placed on insuring that methods and policies for Employee Health and Safety were properly evaluated, implemented, and monitored. The equipment specifications and laboratory areas to be utilized in the 2 MW facility in Golden, Colorado, included a variety of engineering designs and improvements to insure that the OSHA and Environmental regulations are met and greatly exceeded.

Golden Photon has developed a "cradle to cradle" recycling program for handling all of the manufacturing waste materials generated by the two megawatt facility, as well as any modules returned from the field. The establishment of such mechanisms is believed to be necessary in order to ensure maximum recapture and recycling of such waste, consistent with the commitment of Golden Photon as a successful, safe, and environmentally friendly, commercial venture.
Summary and Future Activities

Insuring that the new 2 MW Golden, Colorado, facility has a successful startup is the next milestone necessary to prove a viable commercial venture.

The efficiency results on 4 ft² modules are not quite as expected by this time, however, progress has been made as shown by prototype processing trend lines and distributions. Initial module qualification testing appears successful. In spite of the disruptions due to the transitional effects of relocating/constructing a new facility in Golden, the module processing line and the R&D laboratory efforts are expected to be considerably improved over what has existed in the past. Due to these improvements and the improved understanding of the technology that has been accomplished in 1993, advancement is expected to continue to improve during and after Phase 3 of this subcontract at an accelerated pace.

Major Project Reports


MODULE OUTPUT DISTRIBUTION
(Watts Per 4 Square Foot Module)
(UnEncapsulated)

# OF MODULES IN RANGE

OUTPUT RANGE (Watts/Sq. Ft.)

MODULES TESTED = 27
8/16/92

Figure 1A

AVERAGE MODULE WATTAGE
UnEncapsulated 4FT2 Modules

OUTPUT (WATTS)

BATCH #

# Indicates Number of Modules Averaged

Figure 2

STABILITY RESULTS
Golden Photon CdTe Modules

Relative Output (% of Baseline)

Module #

Days Exposed

Figure 3
Title: Novel Two-Stage Selenization Methods for Fabrication of Thin Film CIS Cells and Sub-Modules

Organization: International Solar Electric Technology (ISET), 8635 Aviation Blvd., Inglewood, CA 90301

Contributors: V.K. Kapur, program manager; B.M. Başol, principal investigator; A. Halani, C.R. Leidholm and A.J. Minnick

The objective of this project is the development CuInSe₂ (CIS) sub-modules of 1 ft² area using novel selenization techniques. In our FY 1991 and 1992 reports we had described the selenization approaches used in this research and provided data on small area devices with up to 12.4% conversion efficiency. CIS sub-modules with 1 ft² area and 3W output were also reported in 1992. During this period of research, we have carried out some fundamental work on CIS film processing and improved the power output of 1 ft² modules to around 6W.

CIS layers and solar cells

Details of the selenization technique and the device fabrication steps used in this work have been previously described [1,2,3]. In summary, the Cu-In precursors were either E-beam evaporated or sputter deposited onto Mo-coated soda-lime glass substrates. Selenization of the precursors was carried out at temperatures ranging from 400 °C to 500 °C in a H₂Se atmosphere to form CIS. Solar cells were completed by the deposition of a thin CdS layer and a ZnO window layer over the CIS film.

During this period an investigation was initiated to evaluate the possibility of adapting certain processing steps used in the co-evaporation technique to the two-stage approach. Specifically, attempts were made to deposit highly Cu-rich CIS films on Mo coated substrates by the selenization technique followed by the deposition of In-rich layers. Such an approach is known to yield very large grain material and high efficiency devices by the co-evaporation method.

Experiments were carried out with CIS films obtained by the selenization of CuInSe₂ precursors at around 500 °C. The Cu/In ratio in these precursors was in the 1.1-1.2 range. The cross sectional SEMs of the selenized films showed a dense layer of 1-2 μm size columnar grains. The lower magnification surface view of the same films, on the other hand, indicated that there was a high aerial density of much larger grains of 5-8 μm size which were imbedded in the matrix of this compact structure. The compositions of the large grains as well as that of the smaller grains were analyzed by EDAX which indicated that while the smaller grain matrix basically consisted of the near-stoichiometric CIS phase, the large grains were almost totally depleted of In. In other words, selenization of a Cu-rich Cu-In precursor film at 500 °C yielded a CIS+Cu₂Se layer with segregated Cu₂Se grains.

Cu₂Se phase segregation in Cu-rich CIS films is expected from the Cu₃Se-In₂Se₃ phase diagram. However, the extent and the form of separation depends on the nature of the film growth
technique. For example, in the Cu-rich films obtained by the elemental co-evaporation process the Cu$_2$Se phase was reported to segregate to the surface areas of the single phase CIS grains during the early stages of deposition. As the thickness of the evaporated film increased, the CIS grains merged together to form a compact columnar structure and the Cu$_2$Se phase totally segregated to the surface of the growing film [4]. This "vertical segregation" of Cu$_2$Se phase in co-evaporated Cu-rich CIS films is depicted in Fig. 1a. It should be noted that the Cu-rich surface in such films can be eliminated by increasing the flux of the evaporated In towards the end of the deposition process. In fact, this is a commonly used approach for growing good quality In-rich CIS films. In the co-evaporation technique the composition of the evaporated flux is continuously adjusted from highly Cu-rich to highly In-rich during the growth period. CIS films prepared by this approach display the large grain size of a Cu-rich material with the desirable electronic properties of an In-rich composition.

Our results with the selenized films pointed to a different form of Cu$_2$Se phase separation. This "in-plane segregation" phenomena may be due to the high mobilities of species during the reaction step of the process and it gives rise to total separation of Cu$_2$Se grains throughout the selenized film as depicted in Fig. 1b. It should be appreciated that such an in-plane stoichiometric non-uniformity in a selenized layer can not be eliminated by reacting this film further with additional In. Therefore, the processing approach described above for the growth of large grain CIS films by the co-evaporation technique can not be readily applied to the selenization method.

The correlation between the CIS film stoichiometry and the solar cell performance can be observed from the data of Fig. 2 which shows a set of illuminated I-V characteristics obtained from a series of 0.09 cm$^2$ area devices fabricated on a glass/Mo/CIS sample with a built-in stoichiometric gradient. A sketch of this substrate, approximate positions of the solar cells and the Cu/In ratios measured by Atomic Absorption Spectrophotometry are also shown in this figure. The I-V characteristics of the devices made on the Cu-rich end of the sample suffer from a high shunt conductance resulting from the segregated Cu$_2$Se regions (curve A). The solar cell parameters gradually improve as the film stoichiometry approaches 1.00. Right on the stoichiometric boundary, we observe cells with open circuit voltage values of 0.3-0.35 V and efficiencies of 5-6% (curve B). The best solar cell performance is found in devices fabricated
on the portion of the substrate corresponding to a Cu/In ratio range of 0.90-0.95 in this specific experiment. The best device of Fig. 2 has an active area conversion efficiency of 12.5 % (curve C). As the stoichiometry becomes more and more In-rich, the fill factors of the devices suffer from a high series resistance (curve D) and eventually a roll-over in the I-V characteristics sets in (curve E) indicating the formation of a rectifier, possibly at the Mo/CIS interface, opposing the main junction of the device.

![Fig. 2 The I-V characteristics of 0.09 cm² area solar cells fabricated on a CIS film with a built-in stoichiometric non-uniformity. Positions of the cells and the approximate Cu/In ratios as determined by AAS are given in the insert.](image)

Sub-Module Processing

Sub-modules measuring up to 1 ft² area were fabricated on soda-lime glass substrates. The first step in the fabrication process was the formation of the back electrical contact. This was accomplished by sputtering a 1-2 µm thick Mo layer on a glass sheet. The Mo layer was then laser-scribed to produce 52 electrically isolated segments measuring approximately 0.5 cm x 30 cm. After cleaning the surface of the substrate, a 100-200 Å thick Te film was deposited on the Mo layer. This was then followed by the deposition of an In and a Cu film using the D.C. magnetron sputtering technique. Selenization was carried out in a reactor that could accommodate multiple 1 ft² substrates. Cell integration was accomplished by a series of film depositions and mechanical scribes as described below.
First a 1000-2000 Å thick layer of CdS was deposited on the CIS layer using the dip coating method. A 2-3 mil wide channel was then scribed in the composite film to expose the Mo contact along the edges of the Mo segments. A layer of doped ZnO was then applied by MOCVD to form the top electrode and to make the electrical connection, through the scribes, with the lower Mo contacts. Module integration was completed by making a final isolation scribe through the ZnO/CdS/CIS layers. Both of the latter scribes were made using a mechanical scribe. Fig. 3 is the illuminated I-V characteristics of a 845 cm² area sub-module measured at NREL. An efficiency close to 7% is a considerably large improvement over the 4% efficient modules we reported in our last annual report.

ISET CdS/CuInSe₂ submodule

Sample: CIS-330
Oct 6, 1993 5:02 PM
Spectrum: ASTM E892-87 Global

Temperature = 25.0°C
Area = 845.2 cm²
Irradiance: 1000.0 Wm⁻²

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Voltage (V)</th>
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<tbody>
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<tr>
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<td>0.0</td>
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<tr>
<td>-0.1</td>
<td>0.0</td>
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</table>

Vₘᵦ = 22.62 V
Iₘᵦ = 0.4626 A
Jₘᵦ = 0.5474 mAcm⁻²
Fill Factor = 55.53%

Vₘₐₓ = 15.60 V
Iₘₐₓ = 0.3724 A
Pₘₐₓ = 5811.1 mW
Efficiency = 6.88%

Fig. 3 Illuminated I-V characteristics of a sub-module measured at NREL. All device parameters are indicated on the figure.

References

Introduction

Siemens Solar Industries (SSI) began a 3-year, 3-phase cost shared contract on May 1, 1991 to demonstrate 12.5% aperture efficient, large area (3900 cm²) encapsulated thin film CuInSe₂-based (CIS) modules. Prior to the contract, SSI demonstrated a 14.1% active-area efficient, 3.4 cm² ZnO/thin CdS/CIS/Mo/glass cell and fabricated monolithic integrated submodules with unencapsulated aperture efficiencies of 11.2% on 940 cm² and 9.1% on 3900 cm² [1]. The best encapsulated large area CIS module power output prior to the contract was 33.7 W, 8.7% aperture efficiency (verified at NREL) over a 3883 cm² area [2].

Objective

Demonstrate large-area, stable 12.5% aperture efficiency CuInSe₂ modules using processes that can be transferred to manufacturing. Success in this effort will be a significant contribution to the DOE Five Year Plan to achieve stable submodules with efficiencies of 15% or more made by scalable, low-cost techniques on inexpensive substrates.

Approach

The module design, illustrated in Figure 1, consists of 53 series-connected ZnO/CdS/CIS/Mo/glass cells fabricated on a 4141 cm² (128.6 x 32.2 cm) glass substrate with a nominal aperture area of 3895 cm² (127.3 x 30.6 cm). The module interconnect region is portrayed in the expanded cross section. Module performance strongly depends on the spatial uniformity of cell and interconnect performance, which in turn depend on the properties of the constituent layers. Emphasis during Phase 1 (FY 92) [3] was on module diagnostics using improved techniques to characterize the cells and interconnects. Siemens Solar started Phase 2 fabricating large area (3900 cm²) modules.
modules pursuing the development of high-performance module processing. The large area parts proved to be a cumbersome test bed for experimentation. A strategic decision was made to utilize smaller substrates (100 cm$^2$) in order to accelerate the progress in solving the types of technical challenges that were discovered in processing large area parts, and to then apply these solutions to larger areas to meet the objectives of the program.

Results and Discussion

The most critical issues determining module yield losses can be grouped into three major categories [4]. The uniformity and reproducibility of the absorber formation process dominates the fundamental performance of the material over a large area. The interaction of the substrate with the films requires appropriate selection criteria and preparation techniques for minimizing defects that lead to shunting and areas of poor photoresponse. Performance losses near interconnects reduce module performance and can cause inadequate performance through module durability testing.

Through the adoption and further refinement of a graded absorber formation process in which the surface layer of CIS incorporates sulfur [5], combined with the appropriately prepared substrate, mean efficiency for 3.3 cm$^2$ test devices was improved from 8.6% to 13.8%, with the best cell efficiency of 16.2%. Figure 2 shows performance distribution for the initial and final processing conditions: note that the cells below 10% efficiency have been essentially eliminated. The I-V curve for the champion cell is shown in Figure 3.

![Figure 2. Performance distribution for baseline process and improved graded absorber process.](image)
Alternate techniques for fabricating interconnects were developed during Phase 2 [6]. In these approaches, the interconnects are made after the formation of the absorber and employ the application of insulating and/or conducting materials (typically polymer-based). The results and interconnect cross-section representations are presented in Figure 4. The 11.7% aperture area efficiency is a record for a CIS-based integrated module and represents significant progress toward meeting the efficiency target for the next subcontract deliverable (11.5% aperture efficiency for an encapsulated 3900 cm² aperture area module).

**Figure 3.** I-V curve of graded absorber device.

**Figure 4:** Module performance for alternate interconnects.
Conclusions and Future Directions

The current focus of the group is to continue to develop techniques capable of meeting remaining contract deliverables by applying lessons learned in Phase 1 and Phase 2 to large area substrates. Key issue of concern are absorber uniformity and process reproducibility, alternate patterning approaches, glass specification, preparation, handling, and coatings, and evaluation of stability. Efforts will continue to address understanding of the mechanisms that control CIS module performance, defining improvements in module design and processing leading to aperture efficiencies of 12.5%.

References


Objective

The overall objective is the demonstration of stable large area thin film CdTe photovoltaic modules fabricated using methods consistent with high throughput manufacturing. Specific goals for the three year program include producing 15% efficient 1 cm² solar cells, 12% efficient 8 cm x 8 cm submodules, and 10% efficient 60 cm x 120 cm modules.

Approaches Taken

SCI utilizes deposition onto hot superstrates from elemental vapors as the method for deposition of the thin films. The vapors are produced by sublimation of heated powders of the compounds - CdS and CdTe. SCI chose this method of fabrication based on its suitability for high speed manufacturing. Films can be deposited at rates in excess of 4 µm per minute. Furthermore, although the precise methods used at SCI are unique, the procedure is similar to Close Spaced Sublimation, a process which has produced 15+% CdTe cells in other laboratories. Further studies involve vapors produced from elemental sources and transported to the superstrate by inert carrier gasses.

Results

During this fiscal year module, submodule and cell efficiencies have all been increased. Confirmed module output, normalized to 1 kW/m², is 53.1 W for a total area efficiency of 7.37% over 7200 cm². Parameters measured at 1043 W/m² were maximum power current, $I_{MP}$, of 848 mA, maximum power voltage, $V_{MP}$, of 65.4 V, and FF 0.596. See Fig. 1. Submodule aperture area efficiency on 64 cm², 8 cell devices reached 9.8% with 828 mV per cell Voc and 0.688 FF. One cm² cell efficiency reached 11.4% with 832 mV Voc, 18.9 mA/cm² Jsc, and 0.725 FF.

A set of modules encapsulated using EVA to laminate to a second piece of glass has successfully passed NREL's Interim Qualification Test Procedure [1]. Similar modules have been assembled and mounted into a nominal 1 kW array erected near the SCI facility in Toledo. See Fig. 2. The array consists of eight panels of three modules each for a total of 24 modules. Initial power output was 931 W. The encapsulation technology employed for this array is not considered to be representative of SCI's final product, nonetheless, after six months output power has declined less than 7%. In separate trials, submodules have been produced which are stable after hundreds of hours of light soaking. This suggests that similarly stable results can be obtained with full size modules.

In order to better understand and control factors influencing module stability, SCI is developing an in-house method for quantifying stability, modeling degradation mechanisms, and predicting module useful life. This program requires a set of 51 modules and involves applying various levels of stress to each one. Stresses include light, temperature, and bias voltage. Analysis will include both empirical observations intended to quantify device degradation and analytical diagnosis of changes in device operation intended to identify the degradation mechanisms. It is hoped that through these studies SCI will be able to make improvements in device structure or processing which will minimize degradation effects and allow us to provide a meaningful warranty to future module users.
Fig. 1  I-V characteristics of a 7200 cm² CdTe module.

Fig. 2  SCI's 1 kW array of CdTe thin film modules located near the SCI facility in Toledo, Ohio.
In additional work, CdTe and CdS films were deposited from elemental vapors transported by nitrogen gas. The ambient pressure ranged from 60 to 600 torr. These experiments demonstrate the viability of depositing II-VI films at atmospheric pressure and point the way toward simplified deposition apparatus and improved control over deposition parameters.

Conclusions and Future Work

Progress continued in FY93 as SCI refined its processing parameters and demonstrated that device quality films can be deposited in apparatus compatible with high throughput manufacturing. In fact, small area devices produced from films deposited in the large system exhibited properties superior to those deposited by CSS in our small chamber. This suggests that further improvements in module efficiency can be expected as the process is further refined. An analysis of factors limiting device efficiency [2] suggests that module output power can reach 85 watts. This would require that we use thinner CdS and an A/R coating to increase Jsc to 22 mA/cm² while achieving the FF (0.72) and Voc (830 mV) that have already been obtained on cells. Improved efficiency will be a significant goal of the third phase of the subcontract.

In addition, much of the work during the remainder of the subcontract will be devoted to understanding and controlling factors associated with device stability. It is believed that this will involve primarily studies of the back contact region and possible modifications to the device structure.

References


Published Papers


Title: Research on Polycrystalline Thin Film Submodule Based on CuInSe₂ Materials

Organization: Solarex Corporation, Thin Film Division
826 Newtown-Yardley Road, Newtown, PA 18940

Contributors: R.R. Arya, Program Manager and Principal Investigator; T. Lomasson, S. Wiedeman, L. Russell, J. Kessler, S. Skibo and J. Fogleboch

Introduction

The objective of the three year cost-shared research program at Solarex is to develop all pertinent processes and technologies required for low cost, high performance copper-indium-diselenide (CIS) modules. In order to achieve the goal of 12% CIS module (FY 1993), we have focussed our efforts on four tasks: (I) Window Layers, Contacts, Substrate; (II) CIS Absorber Layer; (III) Device structure and (IV) Submodule Design and Encapsulation. In each task we have concurrently addressed (a) basic material improvements, (b) fabrication and characterization of CIS solar cells and (c) scale-up of processes to large area substrates.

Major accomplishments within these tasks are:

• Development of ZnS by chemical bath deposition (CBD) as an alternative to CdS.
• Scale-up of CdS and ZnS by CBD to 12" x 13" substrates.
• Scale-up of Mo deposition to 12" x 13" substrates.
• Exploration of elemental and binary metal precursors for CIS formation.
• Scale-up of CIS to 8" x 8" substrates.
• Completion of an integrated laser / mechanical scribing station.
• Completion of Phase I of large area CIS machine - Phase II under construction.

The following sections describe the progress made in each task:

Task I: Window Layers, Contacts, Substrate

The window layer consists of two thin films: (i) a thin CdS or ZnS junction layer and (ii) a ZnO layer. The CdS or the ZnS layer is deposited by CBD process and the ZnO layer is deposited by low-pressure chemical vapor deposition process (LPCVD). The optical transmission in CdS is controlled at short wavelengths by the properties and thickness of the film. As the film thickness decreases there is a corresponding increase in short wavelength response as shown in Figure 1. The optical transmission of ZnO beyond 1000 nm deposited either by rf sputtering or by LPCVD is dominated by free carrier absorption. The optical absorption of LPCVD films increases with thickness, deposition temperature and dopant concentration. The optical transmission of LPCVD deposited ZnO films as a function of deposition temperature is shown in Figure 2. The overall effect of the window layer on the current in CIS devices is shown in Figure 3 where the quantum efficiency versus wavelength of CIS devices with three different CdS thicknesses and two different ZnO layers is shown. The development of ZnS
junction layer has led to CIS devices with comparable photovoltaic parameters as shown in Table I. The two junction layers CdS and ZnS are both deposited by CBD and have been scaled-up to areas > 1000 cm². ZnO deposited by LPCVD has also been scaled-up to areas > 1000 cm².

Figure 1 Optical transmission of CdS films on glass. Thickness of CdS in samples A,B,C,D is 600 Å, 1000 Å, 3000 Å and 10,000 Å respectively.

Figure 2 Optical transmission of large area ZnO films on glass for various LPCVD temperatures.

Figure 3 Quantum efficiency of CIS devices using 400 Å, 500 Å and 1000 Å of CdS (denoted C-1, C-2, C-3 resp.) and similar devices using 10 sccm dopant flow in the ZnO (Z-1) and 30 sccm dopant flow (Z-2).

Table 1 A comparison of CIS devices using either ZnS or CdS as the junction layer.
Task II: CIS Absorber Layer

Elemental deposition and compound formation (EDCF) and an analogous process using copper and indium selenides have been pursued for CIS formation. A large number of elemental and binary precursors, tabulated in Table II, have been investigated. Good precursor morphology was obtained by using a co-sputtered 70/30 Cu/In mixture to produce the gamma phase in the Cu/In system. Low melting metals like indium and particularly gallium have also been sputtered from targets alloyed with copper (In/Cu and Ga/Cu). The binary precursors evaluated for CIS formation are tabulated in Table III. The CIS formed with these precursors exhibited better morphology and better adhesion to Mo coated substrates. The precursors were converted to CIS by heating between 350°C - 550°C from times ranging from 5-60 minutes, usually in the presence of excess selenium. Large area CIS deposition system shown in Figure 4 is under construction. Phase I is completed and work on phase II is underway.

<table>
<thead>
<tr>
<th>Table II</th>
<th>Elemental and binary metallic precursors which has been evaluated at Solarex.</th>
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</table>

| Table III | Precursors using binary metal selenides to form CIS. |

<table>
<thead>
<tr>
<th>1st Layer</th>
<th>2nd Layer</th>
<th>3rd Layer</th>
<th>Heat Treatment</th>
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</thead>
<tbody>
<tr>
<td>Cu</td>
<td>In</td>
<td>Se (solid)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>In</td>
<td>Se (solid)</td>
<td>Cu</td>
</tr>
<tr>
<td>Cu/In (repeating multilayer)</td>
<td>Cu</td>
<td>Se (solid)</td>
<td>In</td>
</tr>
<tr>
<td>Cu</td>
<td>In</td>
<td>Se (solid)</td>
<td>Cu</td>
</tr>
<tr>
<td>Cu</td>
<td>In</td>
<td>Se (vapor)</td>
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<td>Cu</td>
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<td>Se (vapor)</td>
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<tr>
<td>Cu</td>
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<td>Se (vapor)</td>
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<tr>
<td>Cu</td>
<td>In</td>
<td>Se (vapor)</td>
<td></td>
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</table>

Figure 4 Schematic representation of large area CIS deposition system under assembly at Solarex. Elements denoted as phase I are operational, phase II elements are assembled with all major components.
Task III & IV: Device Structure and Submodule Design

Module fabrication procedures have been set up for the device structure:

Light => ZnO / CdS / CIS / Mo / metallic interlayer / soda-lime glass

**Figure 5** shows a schematic of an integrated laser/mechanical scribing station capable of scribing modules with areas over 1000 cm$^2$. **Figure 6** shows a picture of a completed CIS submodule (8" x 8") in which all the layers and all the scribing was done at Solarex.

![Figure 5 Integrated laser and mechanical scribe station.](image)

![Figure 6 Photograph of large area CIS module processed](image)

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Title: Polycrystalline Thin Film Cadmium Telluride Solar Cells Fabricated by Electrodeposition

Organization: Department of Physics, Colorado School of Mines
Golden, Colorado 80401

Contributors: J.U. Trefny, T.E. Furtak, and D.L. Williamson, co-principal investigators; D. Kim, research assistant professor; S. Pozder, B. Qi, and Y. Zhu

Objectives

The main objective throughout all phases of this project, which began on March 20, 1992, is the development of techniques for the growth of high-quality thin films and devices. The research builds upon work performed at Ametek corporation until about 1990 when the laboratory knowhow and equipment were transferred to Colorado School of Mines (CSM). The intent at CSM is to build upon the Ametek experience and expertise regarding polycrystalline, thin-film, CdTe n-i-p solar cells to improve certain processing steps and the potential for economic, large-scale production.

Sample Preparation

Cells with a test structure of glass/SnO\textsubscript{2}/CdS/CdTe/Au and with an area of 0.03 cm\textsuperscript{2} were fabricated using the following procedure. Sodalime glass substrates coated with SnO\textsubscript{2} (Nippon Sheet Glass) were cut into 2" x 3" pieces. The SnO\textsubscript{2} layer was 0.4 µm thick and had a sheet resistance of about 10 Ω/sq. The CdS layers were deposited by chemical bath deposition (CBD). The CdS films were spun coated with a CdCl\textsubscript{2}-EOH solution and dried in air before being put into a furnace. They were then annealed at 450°C for 50 min in a nitrogen atmosphere and cooled in the furnace. The CdTe layers were made by electrodeposition. A split anode consisting of Cd and Te metals was used. The deposition potential was measured between the working electrode and a saturated calomel electrode. All other experimental conditions were similar to those described by Panicker et al.\textsuperscript{1} CdTe films having a thickness of 2 µm were grown in about two hours. A post-deposition anneal of the CdTe was done at 410°C for 45 min in air following a CdCl\textsubscript{2} treatment similar to that described above. The samples were then rinsed with water and etched in a 0.1% Br-MeOH solution for 30 seconds before Au metallization in vacuum. For small-angle x-ray scattering (SAXS) measurements, thin Si wafers (70 µm thick) coated with ZnO were used as substrates for the CdS deposition.

Results and Discussion

SAXS measurements have been made in order to investigate microstructure of thin films. A CdS film of 1000Å thickness showed strong scattering as is shown in Fig. 1(a). Interpretation of this result is complicated by scattering due to grain boundaries and surface roughness. Multiple diffraction involving several grains is also a possibility. One must carefully take these mechanisms into account in order to obtain the correct interpretation. Fig. 1(b) shows the size distribution assuming that the scattering is solely from spherical scattering centers. The scattering signal shifted to smaller angles and the integrated signal increased after annealing, indicating that both the size and the total volume fraction of the scattering centers become larger as a result of heat treatment.

In order to measure the surface roughness, scanning tunneling microscopy (STM) was performed on a 1000Å thick CdS film. As shown in Fig. 2(a) the STM signal indicates a
rough morphology. The "peak-to valley" distance is of the order of 500Å which implies that the existence of pinholes in these films is highly probable especially for thinner films. The thickness fluctuations do not seem to be reduced by annealing as is indicated in Fig. 2(b). Also judging from a two-dimensional STM image, the grain size does not seem to have been affected very much by annealing.

CdS films treated with CdCl$_2$ usually reveal white spots with sizes ranging from about 0.5 mm to 5 mm. Films annealed without CdCl$_2$ treatment do not show this feature. These spots are actually conglomerates of dendritic patterns of either Cd metal or some Cd-rich phase, as is indicated by energy dispersive x-ray spectroscopy (EDS) measurements made on the normal CdS and on the white spots. The EDS results are given in Table 1. For some CdS layers, we observed that the whole surface was covered with this dendrite pattern although in some cases the patterns were not very conspicuous.

The white spots may act as shunt paths or blocking barriers (depending on the nature of the junctions that this layer forms with the CdS layer and subsequently with the CdTe layer) and thus cause poor cell performance. We indeed have observed that some junctions made on these CdS layers show low short-circuit currents. The dendritic pattern may also be responsible for the decrease of optical transmittance observed in some CdCl$_2$-treated films. CdCl$_2$ treatment on electrodeposited CdS is reported to improve the light J-V characteristics of CdS/CdTe cells. Our results indicate that it may be only after a proper optimization that one would see a beneficial effect of CdCl$_2$ treatment on CdS made by the CBD method.

From SEM pictures, CdTe layers obtained by electrodeposition seem to be dense and the grains have facets which are usually a signature of good crystallinity. XRD patterns show a highly predominant (111) peak, and it is only after CdCl$_2$ treatment and annealing that the XRD pattern reveals a more randomly oriented grain structure.

Fig.3 shows a conversion efficiency of 10.4% of a dot cell which has a SnO$_2$:F / CdS / CdTe / Au structure (0.031 cm$^2$).

Summary

Solar cells with a SnO$_2$ / CdS / CdTe / Au structure were made in order to investigate the properties of CdS and CdTe layers. CdS layers were made by a CBD method. The surface of 1000Å thick CdS film showed a roughness of 500Å, indicating that the existence of pinholes in these films is highly probable. Annealing with CdCl$_2$ treatment did not change the roughness or the apparent grain sizes. A first attempt to characterize CdS microstructure by the SAXS method has been reported. CdS films annealed after a CdCl$_2$ treatment usually showed white spots with dimensions ranging from about 0.5 mm to 5 mm. These spots were conglomerates of a dendritic pattern of either Cd metal or some Cd-rich phase. CdTe films made by electrodeposition showed a dense, faceted morphology. The best efficiency obtained using the CdS / CdTe / Au test structure was 10.4%.

References


Fig. 1 (a) SAXS pattern obtained from ZnO/Si substrate and with CdS overlying film ($h = 4\pi \sin \varphi / \lambda$; $2\varphi =$ scattering angle, $\lambda = 0.154$ nm). (b) Size distribution of scattering centers as obtained from SAXS measurements on as-deposited CdS and after anneal.
Fig. 2 STM result on a 1000Å thick CdS film. (a) As-deposited and (b) after annealing (measurement done by Mr. H. Moutinho at NREL).

Table I. Comparison of the composition analysis by EDS on two different regions of a CdS film: white spot and normal surface. The surface was coated with Au for SEM image enhancement.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Atomic%, Normal region</th>
<th>Atomic%, White region</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>29</td>
<td>46</td>
</tr>
<tr>
<td>S</td>
<td>37</td>
<td>19</td>
</tr>
<tr>
<td>Cl</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Au</td>
<td>34</td>
<td>35</td>
</tr>
</tbody>
</table>

Fig. 3 Result of light J-V measurement on a CdS / CdTe / Au cell (0.031 cm²). (measurement done by Dr. K. Emery at NREL).
Objectives

The objectives of this program are the quantitative separation of individual loss mechanisms and the characterization of extraneous electron states responsible for excessive forward current in polycrystalline thin-film solar cells.

Collection Efficiency

The difference between a solar cell's internal quantum efficiency and unity was explored in some detail for polycrystalline thin-film cells [1,2]. In general it is desirable to have a wide depletion region, or a large minority-carrier diffusion length, relative to the photon absorption length, so that electric field and diffusion will maximize the photogenerated carriers in the junction current. Diffusion lengths of polycrystalline thin-film cells, however, are often restricted by grain-boundary recombination or the physical thickness of the absorber layer. Additionally, since depletion width changes with bias, collection efficiency may vary somewhat with cell voltage.

Calculated zero-bias collection efficiencies for cells with absorption coefficients comparable to CuInSe₂ and CdTe are shown in Fig. 1. At operating voltages, the dashed line delineating the depletion boundary is shifted to the left, and the collection efficiency may drop by a few percent as one moves leftward on the graph. One result is a modest decrease in photocurrent. A second result is a complication in the J-V analysis, which if ignored can give the appearance of excessively large shunting. CuInSe₂ cells typically have hole densities near $10^{16}$ cm$^{-3}$, where (Fig. 1) the collection efficiency changes by a non-negligible amount with voltage. CdTe hole densities are generally $10^{15}$ cm$^{-3}$ or less, corresponding to the relatively flat sections of the curves.

Time-Dependent Voltage

Several follow-up experiments were conducted on the nearly-universal tendency of CuInSe₂ and CdTe cell voltages to increase by 5 to 40 mV over several decades of time following the onset of illumination [3-5]. A practical consequence of this effect is that characterization curves from a pulse simulator will be somewhat different from those taken with a cw simulator.

Fig. 2 supports the earlier conclusion that the time-dependent voltage is due to the onset of positive voltage, and not the illumination directly. It shows data taken from a Boeing CIGS cell. The magnitude of the voltage increase was measured three different ways: (1) Voltage was held at a range of pre-biases prior to the onset of illumination and the voltage tracked after
illumination; (2) The cell was switched in the dark to a positive constant-current value and the voltage tracked; and (3) The cell was exposed to different illuminations between 0.1 and 100 mW/cm² and voltage tracked following the onset. All measurements, including the one with no light at all, gave the same voltage effect. The proposed interpretation is that when this cell is exposed to biases between 200 and 400 mV there is a group of long-lived traps that are progressively depopulated. Other cells show a pattern similar to that in Fig. 2. For CdTe, however, somewhat higher biases are required to see the effect.

Cell Analysis

Loss mechanisms of approximately 20 individual cells from a variety of fabrication labs and techniques were analyzed during the past year. Detailed measurements of CdTe cells focused on a series high-efficiency cells made at the University of South Florida [6]. These cells showed considerable progress in reduction of the forward recombination current and a lessening of difference between light and dark forward currents.

With CuInSe₂ cells, an exciting development in junction properties is shown in Fig. 3. This cell, made at NREL, shows nearly perfect superposition of the light (open circles) and dark (filled circles) curves in the operating range. If the variation of collection efficiency with voltage described above is included (open triangles), the superposition is still more impressive. Additionally, this cell has very low values for diode quality factor (about 1.2) and series resistance (between 0.1 and 0.2 ohm-cm²), essentially no dispersion in capacitance, and no measurable time-dependent voltage.

References

Fig. 1. Calculated collection efficiency of typical cells as a function of depletion width, or hole density. $L_{\text{eff}}$ is the effective diffusion length.

Fig. 2. Magnitude of voltage change after bias is switched using three separate techniques.
Fig 3. Superposition of light and dark J-V curves for NREL CuInSe₂ cell M1201-14#4.
**Objectives**

The principal objective of the research project is to develop processes for the fabrication of cadmium-telluride, CdTe and copper-indium-gallium-diselenide, Cu(In_{1-x}Ga_x)Se_2 polycrystalline-thin-film solar cells using techniques that can be scaled-up for large-scale economic manufacture.

**Technical Approach**

Magnetron-sputtered Cd and Te layers are being studied for CdTe-solar-cell fabrication. Two-stage selenization of Cu-In-Ga thin films using selenium vapor is being studied for Cu(In_{1-x}Ga_x)Se_2-solar-cell fabrication so as to avoid the use of extremely toxic H_2Se. Residual stress in Mo coatings is being minimized by optimizing the sputtering conditions. FSEC has established a laboratory for research and development on polycrystalline-thin-film solar cells.

**CdTe Polycrystalline-Thin-Film Solar Cells**

The structure of CdTe thin-film solar cells consisted of glass/SnO_2:F/CdS/CdTe/back contact. Optimum conditions for growth of conformal 500-2500 Å thick CdS heterojunction-partner layers for CuInSe_2 and CdTe thin-film solar cells were cadmium salt concentration Q of 0.002-0.003 M, thiourea concentration 10xQ, ammonium salt concentration 10xQ, pH \~9.15, deposition temperature of \~85° C and deposition time of 6-30 min [1,2]. Elemental layers of cadmium and tellurium were deposited by magnetron-sputtering followed by interdiffusion, CdTe phase formation, and grain growth. Parameters for heat treatments were optimized to minimize the loss of tellurium and cadmium during heat treatment of Cd/Te multilayers. Use of vacuum-melted sputtering targets, efficient water cooling, and good thermal and electrical contacts improved controllability, repeatability, and efficiency of the sputter-deposition from tellurium targets. At present, low deposition rates of \~0.2 \mu m min^{-1} are employed to permit manual deposition control. However, the time for deposition of Cd and Te layers in a 4 \mu m thick CdTe thin film could be reduced to 5-7 minutes. Type and cleanliness of substrate, and adhesion and compactness of individual Cd and Te layers were found to influence the adhesion, and formation of pinholes in heat-treated CdTe thin films. Uniform 2-6 \mu m thick CdTe films were obtained by heat treatment of Cd/Te multilayer structures on glass/SnO_2:F/CdS substrates in partially-closed graphite crucibles in an evacuated quartz tube at N_2 pressures up to 300 Torr. Ramp rate during heat treatment was limited to 20° C min^{-1} to avoid peeling off of CdTe layers especially on plain glass substrates. Blister formation on CdTe films was avoided by limiting the maximum temperature during heat treatment to 400° C. However, samples showed a few pin-holes. X-ray diffraction (XRD) studies showed good CdTe compound formation with highly crystalline, single phase thin...
Fig. 3.  RBS spectra of a Cu\text{In} bilayer before and after heat treatment together with a simulated spectrum.

Fig. 4.  Photograph of six Cu(In$_{1-x}$Ga$_x$)$_2$Se$_2$-thin-film solar-cells
Fig. 1. X-ray diffraction pattern from a CdTe thin film formed by heat treatment of Cd/Te layers on glass/\text{SnO}_2:F/CdS substrate.

Fig. 2. SEM photograph of a CdTe sample after chloride treatment.
**Title:** Development of High Efficiency CdTe Solar Cells

**Organization:** School of Electrical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

**Contributors:** A. Rohatgi, H.C. Chou, A.K. Bhat, S. Kamra

**Objective:** The objective of this program is to improve the basic understanding of efficiency limiting mechanisms in polycrystalline CdTe cells and provide guidelines for achieving high efficiency CdTe cells.

**Cell fabrication**

Polycrystalline CdTe films of thickness 2.6 µm were grown by MOCVD on CdS/SnO2/glass substrates to fabricate the solar cells. The CdS films were made using the solution growth technique. The Te/Cd mole ratio in the growth ambient was varied in the range of 0.02 to 15 by controlling the carrier gas flow rates and the temperatures of the metalorganic sources. After the CdTe deposition, some of the structures were treated with CdCl2-methanol solution and annealed at 400°C in air for 30 minutes. Certain other samples were annealed at temperatures up to 700°C using the Rapid Thermal Processor. Ohmic contacts were formed on the CdTe surface by sequentially evaporating 100 Å Cu and 400 Å, and annealing at 150°C in Ar ambient. Cell fabrication was completed by etching the CdTe surface in 0.1% Br2:CH3OH to remove residual surface oxides.

**Results and discussion**

(a) **Rapid thermal annealing of CdS/CdTe films:** Treatment of CdS/CdTe films with CdCl2-methanol solution followed by a 30 to 50 minute anneal at 400°C in air has been routinely used by several groups to produce polycrystalline CdTe solar cells with efficiencies exceeding 10%. Although the post-growth CdCl2 treatment is believed to enhance grain regrowth and significantly improve cell performance, efficiencies produced to date are below the theoretically projected value of ~18% for the polycrystalline CdTe solar cells. Amongst the possible limiting factors are: 1) defects due to the presence of an excessive amount of Cl, and 2) undesirable diffusion related defects at the CdS/CdTe interface during the long annealing duration. A study, using DLTS measurements, conducted in order to reveal the potential efficiency limiting defects due to the CdCl2 treatment, has been reported earlier. The DLTS measurements showed that, after the CdCl2 treatment, recombination in the depletion region occurs through a large density of deep acceptor-like states at Ev + 0.64 eV which could result from the formation of Cd-vacancy related defects during CdCl2 treatment. Traps in the vicinity of Ev + 0.6 eV have been attributed to VCa and VCa-Cl related complexes. In order to avoid these possible deleterious effects, we are currently exploring the use of RTP for enhancing the cell performance by using annealing temperatures as high as 700°C to achieve grain
regrowth without using CdCl₂ as a fluxing agent.

An efficiency of 10.7% was recorded using RTP in a controlled ambient consisting of a mixture of 7% O₂ in N₂. Secondary Ion Mass Spectrometry (SIMS) was done to confirm the presence of a relatively low level of Cl in the CdTe film (Figure 1). The small traces of Cl in the film are attributed to the CdCl₂ treatment of the CdS film. Preliminary Electron Beam Induced Current (EBIC) measurements made at NREL indicate that the diffusion length of the charge carriers in the RTP cells and the cells that were made using the regular furnace treatment are comparable. We believe that the quality of as-grown films and the CdS/CdTe interface is very critical for RTP cells, and the cell performance can be further improved by carefully monitoring the effects of cell exposure to the ambient air in-between the various processing steps.

(b) Effect of various process parameters on cell performance: A number of process parameters such as concentration of thiourea and CdCl₂ in the solution growth of CdS films, temperature during H₂ treatment of the CdS films, Te/Cd mole ratio during MOCVD growth of CdTe, and the evaporation rates and thicknesses of Cu and Au contact films were varied to study their effect on cell performance. Some of the observations are discussed below.

Oxygen in CdS grain boundaries is known to be a detrimental recombination center. Heat treatment of the CdS films in H₂ ambient in the MOCVD reactor, prior to CdTe deposition, is routinely done in order to remove oxygen and oxygen related defects. It was reported earlier that the treatment also leaves Cd-deficient region on the CdS surface, and it was therefore felt that the temperature used for the heat treatment should be optimized to ensure that the CdS films are stoichiometric. Starting with different solution grown CdS films, a series of experiments were performed to investigate the effect of the temperature on cell performance.

One set of the CdS films chosen was grown using a thiourea concentration of 0.01 M (thiourea rich) and a CdCl₂ concentration of 0.002 M. Another set of CdS films were grown at a slower rate using both thiourea and CdCl₂ concentrations of 0.002 M. It was observed that the optimum temperature depends on the conditions under which the CdS films are prepared. Specifically both Vₐₜ and fill factor were highest (Fig. 2) when the annealing was done at 425°C for films that were grown using a thiourea concentration of 0.01 M. However, for CdS films grown using a thiourea concentration of 0.002 M (slow growth and possibly Cd-rich films), the fill factor and efficiencies improved as the temperature was increased to 475°C. This result is consistent with our earlier conclusion that the heat treatment in H₂ ambient drives out some Cd along with O from the surface.

Some additional studies currently being made on the metallic contacts to CdTe indicate that the diffusion of Cu from the contact into the bulk of CdTe depends on the thickness of the Cu films and the rate of evaporation of Cu. The cell performance appears to be influenced by the diffusion of Cu, and more experiments are planned to study this effect.
Photocurrent loss due to absorption in CdS window layer and multiple beam interference in CdS/SnO₂ films: The simulated photocurrent loss due to absorption in the CdS window layer as a function of CdS film thickness is plotted in Figure 3. It is apparent from the figure that a thin CdS film is desirable in order to minimize losses in the window layer. However, since multiple beam interference in the CdS/SnO₂ layer can affect the reflectance of the solar cell, detailed calculations were made to investigate the impact of CdS thickness on the reflectance and the corresponding loss in photocurrent.

Simulations of reflectance from the cells were made for a fixed SnO₂ film thickness of 10000 Å, and CdS film thickness in the range of 100 Å to 3000 Å. It was found that the loss due to reflectance is very sensitive to the CdS film thickness particularly for thicknesses of less than 1500 Å, and the loss is minimum at a thickness of ~600 Å (Figure 3). In order to partially verify the above projections, the reflectance of two CdTe solar cells with 650 Å and 1600 Å thick CdS layers was measured. The results of the measurements were in good agreement with the results of the simulations.

Figure 3 also shows the combined effect of losses due to absorption and reflectance. It is apparent than theoretically the loss can be minimized by reducing the CdS thickness as much as possible. However, it is worth noting that reducing the CdS thickness below 600 Å does not lead to any significant gain in current. Moreover, very thin CdS may even cause problems due to pin-holes and non-uniformity. Therefore, even though the CdS film thickness should be as small as possible theoretically, the optimum CdS thickness seems to be 600 Å for achieving high efficiency in practical CdTe solar cells.

Conclusion

A study was made to substitute the conventional furnace treatment of CdTe films by RTP. RTP offers the advantage of grain regrowth without use of CdCl₂ as a fluxing agent. An RTP cell efficiency of 10.7% was recorded in this study. The effect of thiourea and CdCl₂ concentrations in the solution growth of CdS and heat treatment of CdS films in H₂ was studied to obtain guidelines for improving cell performance. The effect of Cu film thickness and evaporation rate on Cu diffusion and cell parameters is currently under study. Additionally, model calculations were made to determine the loss in photocurrent in CdS/CdTe cells due to the CdS window layer.

References

Fig. 1: SIMS data showing low Cl content in RTP CdTe film

Fig. 2: Effect of CdS annealing temperature on (a) $V_{oc}$, (b) fill factor, and (c) cell efficiency for CdS films grown using 0.01 M thiourea (*) and 0.002 M thiourea (+) bath solutions

Fig. 3: Photocurrent loss due to absorption in CdS window layer and reflection due to multiple-beam interference in SnO$_2$/CdS films
Objective

The purpose of this research program is to develop an accurate numerical model for CuInSe$_2$ (CIS) and CdTe based solar cells which can be run on IBM compatibles and Unix-based Sun workstations. The model, ADEPT (A Device Emulation Program and Tool), is used to analyze and aid in the design of CIS and CdTe based solar cells and is being released to the photovoltaic community. Here, results will be presented for simulation of the second junction sometimes observed in CIS solar cells.

Approach

From the low temperature illuminated I-V characteristics of CdS/CuInSe$_2$ diodes, it has been observed that there is a second junction present in addition to the main rectifying junction. However, the location of this junction has not been established. Some observations suggest that the back contact of CIS/Mo is quasi ohmic and that it may develop another junction. Others suggest that the back contact is indeed ohmic and that second junction is present near the CdS/CIS interface. Numerical modeling of these devices can show the nature and the effect of the second junction on the I-V characteristics.

Mo/CIS Schottky Contact

The temperature dependent behavior of the molybdenum/copper indium diselenide (Mo/CIS) rear contact in CuInSe$_2$ based solar cells was investigated[1]. It was proposed that modeling the Mo/CIS contact as a simple Schottky barrier could explain the temperature dependent behavior observed in some CIS based solar cells.

Band Offset Between CdS and CIS

It is generally believed that solar cell performance is little affected if the electron affinity of CdS is larger than that of CIS. Simulation results show that the illuminated I-V at low temperatures is influenced by the conduction band offset. The simulated I-V curves at different temperatures are plotted in Figure 1: The electron affinity of CdS was assumed to be 4.7 eV, while that of CIS was 4.3 eV. The equilibrium band
diagram is shown in Figure 2. As the applied bias becomes comparable to the built-in voltage between CdS and CIS, the fixed $\Delta E_c$ at CdS/CIS interface becomes a potential barrier for electrons (Figure 3). In the intrinsic CIS near the junction, the electrons see potential barriers on both sides and the electrons pile up at the CdS side of the interface. This results in very little change in the current. Since the carrier concentrations increase with applied bias, at some point the piled electron concentration becomes large enough to induce band bending right at the interface and the effective barrier height for electrons is lowered, as seen in Figure 4. This effect is seen only at low temperatures if the difference in electron affinity is small. The same effect can be seen even at room temperature if the conduction band offset is very large. Thermionic emission of carriers over the barrier determines the I-V characteristic, with the current being proportional to $\exp(-q\phi_b/kT)$. A large barrier at room temperature is effectively the same as having small barrier at low temperature, i.e. the electrons lack thermal energy to overcome the barrier.

Summary

It has been shown that the existence of a "second" junction either near CdS/CIS interface or at the back can lead to non-ideal I-V characteristics at low temperatures. Indeed, it is possible that both of these effects may occur simultaneously. Investigation of this and other effects is continuing. Simulation code enhancement is continuing as well.

Reference

Figure 1. Simulated I-V characteristics at various temperatures showing the presence of a second junction at the CdS/CIS interface. No second junction is apparent at room temperature.

Figure 2. Equilibrium band diagram for CdS/CIS solar cell.
Figure 3. Energy band diagram with applied bias of 0.65 V. Note the presence of a second junction at the CdS/CIS interface.

Figure 4. At large bias, the concentration of piled up electrons at the interface is large enough to cause the band bending in the CdS.
Title: Novel Thin-Film CuInSe₂ Fabrication

Organization: University of Colorado, Boulder

Contributors: A. M. Gabor and A. M. Hermann (principal investigator)

Background

The work carried out under this subcontract originally focused on using rapid thermal processing of various precursor layers to form CuInSe₂. It was then discovered at NREL that other precursor reaction schemes held the promise to obtain layers for high-efficiency devices. Thus, it was decided to align the objective with that of the NREL CIS task. The work was integrated in the deposition schemes pursued at NREL, as described below. The thin film fabrication, characterization, and device delineation were carried out at the NREL facilities, and were integrated into the operating plan as part of the NREL CIS team research effort that resulted in world-record breaking Cu(In,Ga)Se₂ solar cells.

Objectives

The major objective during 1993 was to explore new simplified processes for CuInₓGa₁₋ₓSe₂ thin-film fabrication which result in high efficiency cells. Processes can be simplified by separating the deposition of the constituent elements into different stages, and the processes can be designed to take advantage of the properties of the intermediate or secondary compounds that form during the film growth. In addition, films made by such multi-stage processes can have properties that vary as a function of film depth in such a way as to aid cell performance.

Technical approach

The compound CuInSe₂ (CIS) can be represented as a region on a phase diagram connecting the compositions In₂Se₃ and Cu₂Se. Either of these compounds are potential precursors to CIS formation. By using such precursors one can simplify a process by separating the deposition of Cu from the deposition of In. Better cells are known to be formed by alloying CuInSe₂ with the higher band gap CuGaSe₂ to form CuInₓGa₁₋ₓSe₂ (CIGS). With these motivations we chose to explore two different pathways to CIGS formation:

A) Exposure of a Cu-Se precursor film to In + Ga + Se.
B) Exposure of an In-Ga-Se precursor film to Cu + Se.

In process A) we coevaporated Cu and Se at various temperatures and then exposed this precursor to a flux of In, Ga and Se at a substrate temperature Tₛ > 540°C. In process B) we coevaporated In, Ga, and Se at 250 ≤ Tₛ ≤ 300 °C and then exposed this precursor to a flux of Cu and Se at Tₛ > 540°C. The finished films were characterized by xray diffraction spectroscopy, various
compositional analyses, and scanning electron and atomic force microscopy. The films were made into devices with the structure as shown in Fig 1.

Results

Figure 2 shows the J-V curves and total-area cell parameters for the best CIS and CIGS devices made by process B), as independently measured at NREL. The total-area efficiency of 13.2% is the highest official measurement for any CIS solar cell, and the total-area efficiency of 15.9% for CIGS is the highest official measurement for any non-single-crystal thin-film solar cell. The cells made by process A) were not impressive by comparison.

The films made by the two processes were remarkably different (see Fig. 3). In process A) the finished films had very large grains but were rough to the point of having voids between grains in some cases. Such voids will short devices. The grain growth is likely promoted by excessive amounts of a liquid Cu$_x$Se phase which is consumed as the (In,Ga) is added.

In process B) the precursors were of the composition (In$_x$Ga$_{1-x}$)$_2$Se$_3$ and were specularly smooth. This smoothness was largely retained in the finished films and might contribute to device performance by keeping down the dark current and the density of interface states per unit projected area. The Ga content in the CIGS films can vary as a function of film depth, which means that this process can produce graded bandgap structures to aid device performance.

Physical vapor deposition was used to deposit the elements, but in concept the process should work using what may be the more scalable techniques of sputtering or electrodeposition of the elements or compounds.

Conclusions

We have developed in conjunction with researchers at NREL a new process for CIGS thin film formation. Record efficiency devices were made using this process. The process variables lend themselves toward engineering different device structures, and scalability of the process appears promising.

Publications

3µm Al
1250Å MgF2
500Å Ni
3500Å conductive ZnO
500Å resistive ZnO
500Å CdS
2.5µm CIGS
1 µm Molybdenum
soda-lime glass

Figure 1  The cell structure.

Figure 2  The J-V curves for the best CIS and CIGS cells made using the (In_x,Ga_{1-x})_2Se_3 precursor process.

<table>
<thead>
<tr>
<th></th>
<th>CIS</th>
<th>CIGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area (cm^2)</td>
<td>0.395</td>
<td>0.437</td>
</tr>
<tr>
<td>Voc (V)</td>
<td>0.484</td>
<td>0.649</td>
</tr>
<tr>
<td>Jsc (mA/cm^2)</td>
<td>36.29</td>
<td>31.88</td>
</tr>
<tr>
<td>FF (%)</td>
<td>75.10</td>
<td>76.60</td>
</tr>
<tr>
<td>Eff. (%)</td>
<td>13.2</td>
<td>15.9</td>
</tr>
</tbody>
</table>
Figure 3  SEM micrographs of CIGS films made from a) a Cu$_x$Se precursor, and b) an (In$_x$Ga$_{1-x}$)$_2$Se$_3$ precursor.
Title: Processing and Modeling Issues for Thin Film Solar Cell Devices

Organization: University of Delaware
Institute of Energy Conversion
United States Department of Energy
University Center of Excellence
For Photovoltaic Research and Education
(National Renewable Energy Laboratory)
Newark, DE 19716-3820

Contributors: Robert W. Birkmire and James E. Phillips, principal investigators; Wayne A. Buchanan, Steven S. Hegedus, Brian E. McCandless, William N. Shafarman, Tracey A. Yokimcus

OBJECTIVES

The objectives of this research are to obtain an understanding of the materials processing, properties and performance of polycrystalline CuInSe₂ and CdTe as well as a-Si thin-film solar cells needed to achieve the goals for efficiency, reliability and cost for flat plate thin-film photovoltaic systems set by DOE for the National Photovoltaics Program. A further objective of this program is to support the development of a competitive U.S. photovoltaic industry through collaboration with other research groups and the training of photovoltaic engineers and scientists.

TECHNICAL APPROACH

In its effort to help the photovoltaic community to achieve commercially viable solar modules, the Institute of Energy Conversion (IEC) is concentrating on developing, implementing, and analyzing laboratory experiments which provide essential information for the manufacture of large-area photovoltaic modules. To do this effectively, the Institute’s multi-disciplinary team of physicists, material scientists and electrical and chemical engineers work together in an integrated approach encompassing: Materials synthesis, Process Equipment Design and Operation, and Device design and analysis.

The items addressed in this work are:

1. Chemical reaction and reactor analysis for copper indium diselenide formation in a flowing H₂Se reactor.
2. Device analysis and comparisons of CuInSe₂ and CuIn₉₋ₓGaₓSe₂ solar cells made by various methods and manufacturers.
3. Analysis of the effects of the post-processing CdCl₂, O₂ and Cu treatments on CdTe/CdS solar cells.
4. Description and initial results of IEC’s collaboration with NREL a-Si research teams.
RESULTS

This is a report on Phase I of a three year phased research program of integrated investigations of processing, properties, and performance of thin film polycrystalline CuInSe$_2$ and CdTe and amorphous Si based solar cells.

1. CHEMICAL REACTOR AND REACTION

IEC has three laboratory scale reactors which produce photovoltaic grade CuInSe$_2$:

- A four source physical vapor deposition reactor (Cu,In,Se,Ga)
- A single source physical vapor deposition reactor (Se) to selenize copper/indium/gallium layers
- A tubular continuous flow chemical vapor deposition reactor to selenize copper/indium/gallium layers with H$_2$Se and Se.

A reaction analysis seeks to obtain a quantitative description of the molecular phenomena of the system of interest. This requires the following: identifying chemical species, determining chemical equations, expressing reaction rates, and obtaining specific reaction rate constants and activation energies from well designed experiments. Reaction analysis is an essential element of the more complicated problem of predicting electronic properties and eventually device performance.

A reactor analysis seeks to obtain quantitative descriptions of the transport phenomena critical to reactor design and operation. Delivery of raw material to the growing polycrystalline film must be modelled and predictions must be verified experimentally so that the design of a commercial scale reactor can be carried out effectively.

Reactor Analysis

Reactor analysis of an atmospheric, flowing gas system is complex since the fluid dynamics of delivering the gas species depends on the system geometry and, possibly, gas phase reactions. A reactor analysis is simpler to carry out on the physical vapor deposition reactor and IEC has pioneered such research.

This can be readily done with existing engineering procedures once the geometry of the reactor is specified. In our judgment it is possible at the present time to design a commercial scale physical vapor deposition reactor which will produce high quality thin films of CuInSe$_2$ in areas large enough to make modules on the order of a square meter. However, to optimize such designs and achieve minimum capital and raw material costs with flexible, low cost operation may all require experimentation at a level of pilot plant scale. Whether it is desirable to co-evaporate all components or to selenize copper indium layers requires very detailed equipment design for both physical vapor deposition reactors and careful cost analysis.

Reaction Analysis

To carry out a complete reaction analysis, we need experimental measurements of species concentration as a function of time. This can only be done in our tubular reactor since the reaction can be stopped at any time by discontinuing
the gas flow and physically removing the sample from the reaction zone. An extensive series of experiments for making CuInSe$_2$ films has been carried out in a tubular reactor with flowing 3.4% H$_2$Se in argon. It is experimentally difficult to stop the physical vapor deposition reactors quickly because they require long times to cool.

2. DEVICE ANALYSIS OF CuInSe$_2$ AND CuIn$_{1-x}$Ga$_x$Se$_2$ SOLAR CELLS

CuInSe$_2$ Solar Cells

For this study, J-V characteristics have been measured as a function of temperature and light intensity for a variety of CuInSe$_2$/CdS solar cells. This includes cells fabricated at IEC which had the CuInSe$_2$ deposited by evaporation and selenization, as well as cells fabricated by Siemens Solar Industries (SSI), Energy Photovoltaics, Inc. (EPV), and the Institute for Physical Electronics at the University of Stuttgart.

J-V data for the six CuInSe$_2$/CdS solar cells fabricated by different techniques at different laboratories were analyzed to determine the junction properties and compared for the different devices. Since all the cells have non-linear contributions in series with the main diode, the diode quality behavior is determined from the results at $V_{oc}(J=0)$ where these series effects do not contribute. The devices all have the same general diode behavior described by a standard diode equation with barrier height of 1.0 eV and diode quality factor near 1.5 over the entire range of temperature and intensity.

CuIn$_{1-x}$Ga$_x$Se$_2$ Solar Cells

Measurements and analysis of J-V data show that CuIn$_{1-x}$Ga$_x$Se$_2$/CdS solar cells with Ga contents up to 30% ($x=0.3$) have the same simple diode behavior that has been observed and described for devices without Ga. This specifically includes the fact that the activation energy or barrier height, $E_a$, determined from J-V measurements corresponds to the optical bandgap of the material. Measured barrier heights, $E_a$, equal to the bandgap of the CuIn$_{1-x}$Ga$_x$Se$_2$ combined with diode quality factors in the range from 1 to 2, suggest that the J-V behavior of these devices is controlled by Shockley-Read-Hall recombination in the CuIn$_{1-x}$Ga$_x$Se$_2$ layer.

Table 1. Activation energy ($E_a$), diode quality factor ($A$), and $J_{oo}$ from $V_{oc}$, $J_{sc}$, and temperature measurements

<table>
<thead>
<tr>
<th>Device</th>
<th>CuInSe$_2$</th>
<th>CuIn$<em>{0.7}$Ga$</em>{0.3}$Se$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (eV)</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>$A$</td>
<td>1.3</td>
<td>1.5</td>
</tr>
<tr>
<td>$J_{oo}$ (mA/cm$^2$)</td>
<td>4.3x10$^8$</td>
<td>3.4x10$^8$</td>
</tr>
</tbody>
</table>

3. POST-PROCESSING ANALYSIS OF CdTe/CdS SOLAR CELLS

The microstructural properties of evaporated CdTe/CdS layers after CdCl$_2$ treatment were investigated. CdTe recrystallization, grain growth, and CdTe-CdS interdiffusion were determined using x-ray diffraction and scanning electron microscopy of samples treated at 400°C for 2 to 30 minutes. Selected samples
were also analyzed by cross-sectional transmission electron microscopy and spot EDS by M. Al-Jassim at NREL. The results of these analyses are summarized as follows:

1. Significant CdTe recrystallization occurs in 2-5 minutes.
2. CdTe grains re-orient and coalesce independently of the underlying CdS layer.
3. S diffusion into CdTe is progressive with time.
4. The CdTe\(1-x\)S\(x\) layer is compositionally non-uniform.

Analysis of the post-deposition process used to fabricate cells shows that the oxygen content of the heat treatment atmosphere and the quantity of Cu present in the contact affect \(V_{oc}\) and FF, leading to \(V_{oc}\) as high as 830 mV on all-evaporated cells. The sensitivity of the devices to oxygen and Cu is believed to reflect the doping level within the CdTe layer. Modifications to the CdTe deposition parameters to allow \textit{in situ} doping may eliminate this sensitivity so that the post deposition treatment will only be necessary to restructure the CdTe/CdS.

4. \textbf{a-Si RESEARCH COLLABORATION}

IEC participates in two of the NREL Multijunction Research Teams, the Low Bandgap Team and the Device Design and Interface Team. We have provided films, devices and results to researchers in the Low Bandgap and Stability Teams leading to several publications by those groups.

Our contribution to the Low Bandgap Team was to study effect of i-layer grading on the performance and stability of a-SiGe p-i-n devices using bifacial QE(V) and FF measurements with strongly absorbed blue light. We found that the primary benefit of grading the a-SiGe in the front-loaded i-layer design is improved hole collection. Electron collection degrades more than hole collection after 200 hours light soaking leading to comparable electron and hole collection.

IEC also plays a major role in the Device Design and Interface Team since it is one of the two University groups which can fabricate devices and test structures. Our efforts included studying TCO/p-layer interfaces and tunnel junctions using special test structures rather than p-i-n devices.

These interconnections between cells in a monolithically integrated multijunction device form a reverse biased p-n junction, often referred to as a tunnel junction. They are required to pass current with a negligible voltage drop to maintain a high \(V_{oc}\), to have negligible absorption to maintain high \(J_{sc}\), and to be ohmic, not rectifying, to maintain high FF. IEC has assisted APS, Inc. in evaluating various tunnel junction structures. Structures fabricated at both labs confirmed the improvement seen with a thin (<40Å) highly doped a-Si p-layer (not a-SiC) inserted between the regular p and n-layers. This layer "shorts out" the junction; i.e. enhancing recombination by supplying holes. It has negligible absorption loss, making it a practical solution to improve tunnel junctions.
Objectives

The objectives of this project are to study the effect of the substrate temperature for the deposition of CdTe films by the close spaced sublimation (CSS) on device performance, and the fabrication of high efficiency CdTe/CdS solar cells at low temperatures using inexpensive glass substrates.

Film growth

The CdTe films were deposited by the CSS. The substrate temperature and total reactor pressure were varied in the ranges of 450-600°C and 1-50 torr respectively. The source and substrate spacing was varied from 2 to 10 mm. Three deposition processes were used for the deposition of the CdS films on the SnO\textsubscript{2}/glass substrates: chemical bath deposition (CBD), close spaced sublimation (CSS), and sputtering. The CBD of the CdS films is carried out at a temperature of about 90°C. A detailed description of this process has been previously reported\cite{1}. The CBD CdS films are highly resistive and consist of very small grains (<0.1\mu m); a heat treatment is required to enhance the grain size and lower the resistivity of the films. We have recently started investigating the properties of CdS films prepared by the CSS and sputtering techniques, and begun using some of these films for solar cell fabrication. Substrate temperatures well above 100°C are being used for both of these processes. The grain size of these films is typically larger than that of the CBD films (on the order of 1\mu m) and depends on the deposition conditions. The substrate temperature and the total pressure during the CSS of the CdS films was varied from 400 to 550°C and 1 to 50 torr respectively. The substrate temperature during the sputtering process was varied in the range of 100-350°C and the Ar pressure was about 5 mtorr. During the early stages of this work CdS films prepared by all of the above techniques were heat treated in H\textsubscript{2} prior to the deposition of the CdTe layer. The annealing conditions had been previously optimized for CBD CdS\cite{2}.

Results and discussion

CdTe

Early efforts were focused on lowering the substrate temperature from over 600 °C to less than 500°C, while maintaining relatively fast deposition rates (1-2 \mu m/min). At lower substrate temperatures the CdTe films did not exhibit any preferential orientation such as
that observed at high temperatures[2]. The density of the low temperature films was also
lower than the density of films prepared at high temperatures (>550 °C). Solar cells made
from such films exhibited increased shunting and a drastic reduction in the open-circuit
voltage for temperatures below 540 °C. In order to reduce shunting the CdTe films were
grown to larger thicknesses up to 10 µm. The CSS deposition conditions have been
modified to produce higher density films at low temperatures; typical film thicknesses are
currently about 4-6 µm. Open-circuit voltages as high as 850 mV have been obtained for
films prepared at or below 500 °C. A device prepared at 460 °C exhibited an open-circuit
voltage of 880 mV; this value degraded to less than 860 mV about 48 hours after the first
measurement was made.

Spectral response measurements indicate that the processing temperatures have an effect
on the extent of interdiffusion at the CdTe/CdS interface. Figure 1 shows the QE of two
devices prepared at 500 and 550 °C. The response of the two cells is similar at long
wavelengths. However, the roll off of the high temperature device begins at a longer
wavelength than the low temperature one. These results suggest that the extent of
interdiffusion can be controlled by varying the substrate temperature. Better understanding
of the effect of processing parameters on the interface is expected to lead to further
increases in the open-circuit voltage.

CdS
In order to further enhance our understanding of the junction formation mechanisms, CdS
films prepared by the CSS and sputtering were recently used for the fabrication of solar
cells. Table I lists early results on the open-circuit voltage obtained from such devices on
soda lime and borosilicate glass substrates. Both CSS and sputtered CdS films show
preferential orientation along the (002) axis in the range of deposition conditions used to
date. Even though, annealing in H₂ results in a decrease in the resistivity of the sputtered
CdS films, the same is not true for CSS CdS films which appear to be resistive even after
annealing in H₂. CSS CdS films contain pinholes when they are prepared at small
thicknesses. Considerable improvements in processing have been made to improve the
quality of these films, and a recent device utilizing a CSS CdS layer has produced an open-
circuit voltage of 830 mV, and a fill factor over 70%. These results suggest that CdTe/CdS
solar cells for which both semiconductor layers are deposited by the CSS technique can
achieve high efficiencies. Solar cells prepared using CdS films prepared by sputtering have
also produced high open-circuit voltages up to 830 mV, however, the fill factors of these
devices are much lower. It should be noted that most sputtered CdS films were deposited
on soda lime glass substrates.

The extent of interdiffusion between the CdS and CdTe layers appears to be affected by the
density and grain size of the CdS films. Figure 2 shows the QE of a device prepared with
CSS CdS. The CdTe(CSS) layer was deposited at 600 °C. Unlike the high temperature
device (550 °C) of figure 1 that utilizes a CBD CdS film, the roll off for this cell is much
closer to the CdS edge (510 nm). It appears that the use of CSS CdS limits the formation
of the mixed CdS₁₋ₓTeₓ layer.
Conclusions

Significant progress has been made in improving the properties of CdTe/CdS solar cells prepared using low processing temperatures. Open-circuit voltages of 840-860 mV have been achieved for devices prepared in the low temperature range of 460-500°C. The efficiencies of such devices are currently limited by relatively low fill factors. It is necessary to identify the limiting factors and improve the conversion efficiencies by optimizing certain processing steps. High open-circuit voltages accompanied by high fill factors have been achieved for devices prepared using the CSS process for the deposition of both the CdS and CdTe layers. It may be possible to control the composition of the mixed crystal formed at the CdTe/CdS interface by varying the processing temperatures and the properties of the CdS films. Future activities will focus on further optimization of the low temperature CdTe-CSS process, improvements of the quality of the CSS CdS films, and development of process and device models that will assist in improving the performance of CdTe/CdS solar cells.

CIS

Objectives

The objectives of this project are to develop manufacturing-friendly processes for CIS solar cells, to develop understanding of the underlying materials and device mechanisms, and to correlate the performance and processing mechanisms.

Processing and Analysis

During the past year we have made significant progress in development of manufacturing friendly processing for CIS solar cells. That progress can be measured in terms of advances in understanding processing mechanisms as well as in measured performance. Using our least controlled, and therefore most manufacturing compatible process, we have produced devices with efficiency of order 10% which meets the Phase I objective of our project.

The processing technique which we have been developing for formation of CIS includes two primary steps: 1) deposition of the metal precursors, Cu and In, by sputtering, and 2) selenization using a solid-state source of Se. The selenization step is most sensitive to critical details regarding temperature profiles and the availability of Se during the various stages of those profiles. We have been pursuing two selenization paths in parallel. The first of these allows for the application of controlled Se fluxes at any stage of the anneal profile. This allows separation of bulk and surface formation so that each can be optimized independently. This has been a key requirement for formation of high quality CIS. However, the degree of control which this requires makes manufacturing scale-up more difficult.

Our second and more favored process relaxes control of the Se flux. In this process the Se is "made available" within the reactor and is released according to the details of the anneal profile. Using these processes our good devices have parameters in the following ranges: $V_{oc}: 350-410 \text{ mV}$, $J_{sc}: 35-40 \text{ mA/cm}^2$, FF: .55-.63. Understanding the dependence of these on the processing steps is a key objective of this project. An example of progress in this area is provided in figure 3. Our primary figure-of-merit at this stage is $V_{oc}$ and we have chosen
a device from the literature with a $V_{oc}$ of 455 mV as our objective since its performance (12%) is indicative of state-of-the-art devices (though made using H$_2$Se) not containing Ga. As seen in figure 3 our devices show steady progress toward matching the performance of this device. Our analysis indicates that $V_{oc}$ has been driven upward in part because of a correlation between barrier height and process temperature. Establishing this correlation is very dependent upon understanding of the underlying device mechanisms. The temperature dependence in figure 3 has been interpreted in terms of a model which is currently under development. We have in essence been able to successfully model the temperature dependence of $V_{oc}$ as shown, as well as other discerning attributes of device behavior such as $J_{sc} \cdot V_{oc} \cdot C \cdot V$, and the power curve. A key objective of the next phase of this analysis effort is to understand the interplay between surface and bulk mechanisms.

**ZNO**

The ZnO window layer is also an important element of CIS technology, and we have undertaken further development of its capabilities as well. In particular we have focussed our efforts on deposition of ZnO by reactive magnetron sputtering from a Zn target. This promises to offer much higher deposition rates than sputtering from an oxide target which is again important to manufacturing considerations. For Al doped ZnO we have achieved resistivities in the range 2 - 5 x 10$^4$ Ω-cm with reasonable electronic properties[3]. We are also exploring F doping and are finding that it etches the growing film as well as acting as a dopant. We feel that this may provide an opportunity for further enhancing performance. Film properties are also a function of location relative to the target. We are presently studying these phenomena to improve large area uniformity. Thus far we have maintained good electronic properties up to deposition rates of 9 Å/s.

**Conclusions**

We have accomplished the Phase I efficiency objectives for CIS performance using a minimal control deposition process. A model is under development which explains device behavior and correlates device and processing parameters. Good electronic quality ZnO has been deposited by reactive magnetron sputtering. Further developments from combined use of Al and F doping are expected.

**References**


TABLE I

<table>
<thead>
<tr>
<th>SUBSTRATE</th>
<th>CdS/THICKNESS(Å)</th>
<th>CSS T&lt;sub&gt;SUB&lt;/sub&gt;(°C)</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt;(mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7059</td>
<td>Sputtering/2000</td>
<td>460-480</td>
<td>820-830</td>
</tr>
<tr>
<td>7059</td>
<td>Sputtering/2000</td>
<td>460-480</td>
<td>740-810</td>
</tr>
<tr>
<td>7059</td>
<td>CSS/4000</td>
<td>550</td>
<td>790-800</td>
</tr>
<tr>
<td>7059</td>
<td>CSS/800-900</td>
<td>600</td>
<td>830</td>
</tr>
<tr>
<td>Soda-lime</td>
<td>CBD/600-700</td>
<td>450</td>
<td>830</td>
</tr>
<tr>
<td>Soda-lime</td>
<td>CBD/600-700</td>
<td>570</td>
<td>800</td>
</tr>
</tbody>
</table>

Fig. 1. The spectral response of two CdTe cells prepared at different substrate temperatures.

Fig. 2. The spectral response of a CdTe(CSS)/CdS(CSS) solar cell.

Fig. 3. V<sub>OC</sub> vs. T for a literature device (SSI), and representative USF CIS devices.
Objectives

The principal objectives are the improved understanding of the process of rf sputtering for the deposition of CdTe and CdS polycrystalline thin films and the further improvement of small-area CdTe solar cells grown by this process.

Technical Approaches

At the University of Toledo we have demonstrated that rf sputtering, as well as laser physical vapor deposition (LPVD), can be used for CdS and CdTe film deposition and CdS/CdTe cell fabrication to yield AM1.5 cell efficiencies above 10%.\(^1\),\(^2\),\(^3\) Because rf sputtering is a readily scalable deposition technique, we presently emphasize this method for cell fabrication. The LPVD method continues to be used for deposition of CdCl\(_2\) layers and for exploratory studies of doped and alloyed films. In addition to the work on CdS and CdTe, we have studied this year the sputter deposition of doped ZnTe and ZnO.

During the past year we have examined the dependence of film growth rate and grain size on substrate temperature, rf power, and sputter gas pressure. Other film characterization has been performed using Hall measurements, temperature dependent electrical conductivity, optical absorption, photoluminescence, Raman scattering, x-ray diffraction, scanning electron microscopy and energy dispersive x-ray spectroscopy.\(^4\),\(^5\) In collaboration with scientists at NREL, film microresponse and uniformity have been studied by electron beam induced currents and carrier dynamics have been measured by photoluminescence decay lifetimes.\(^2\) In-house device testing includes I-V measurements and spectral quantum efficiency measurements as well as electroreflectance and photoreflectance. We are beginning optical emission spectroscopy studies of the sputtering plasma for growth diagnostics and control.

We have continued collaboration with Solar Cells Inc and with other NREL-supported groups.

Examples of some of the results obtained during the past 12 months are provided below.
RF Planar Magnetron Sputtering of CdTe, CdS, and ZnTe

Sputtering was performed with a two-inch planar magnetron gun from AJA International using a target-substrate distance of seven cm. The turbo-pumped chamber has a base pressure of \( \sim 3 \times 10^{-7} \) Torr; pressure was maintained at constant flow (\( \sim 15 \) sccm) by an exhaust valve controller.

The dependence of the CdTe and ZnTe growth rates on substrate temperature is shown in Fig. 1. The CdTe films were grown on 10 Ω SnO₂-coated soda-lime glass at 17 mT of Ar and rf power of 120 W; the ZnTe was grown on uncoated soda lime glass at 12 mT and 150 W of rf power. Note that the growth rates decrease rapidly for substrate temperatures near 400°C, presumably due to decreased sticking coefficients.

The growth rates as a function of rf power for CdTe on SnO₂-coated glass and ZnTe on uncoated glass are shown in Fig. 2. The growth rates for both CdTe and ZnTe show a nearly linear dependence on rf power above about 50 W for this 2-inch gun.

Figure 3 shows the growth rate of CdS films vs. sputtering gas pressure with substrate temperature of 325 °C and rf power of 120 W. Note that the growth rate appears to maximize near 6 mT and decreases significantly for higher gas pressures. At 25 °C the mean free path for a typical neutral atom in argon at 6 mT is 7-10 mm so that at the higher pressures, multiple collisions in the gas between the target and substrate will cause the growth rate to decrease.

SEM Studies of Grain Size in CdS and CdTe

The reduction of grain boundary effects in polycrystalline thin films is very important for the improvement of cell performance. Increasing the grain size is one approach to reducing these effects. The effect of post-growth anneal of these LPVD films (without the use of CdCl₂) is shown in Fig. 4. From the data we infer the enthalpy for grain boundary movement in CdS to be 0.94 ± 0.1 eV and in CdTe 0.53 ± 0.07 eV. Thus, the enthalpy for grain growth in CdTe is significantly less than that for CdS, which is consistent with the known bond strengths in these materials.

Photoluminescence Studies of CdS/CdTe Interface Diffusion

As an example of the use of photoluminescence (PL) for PV materials studies, Fig. 5 shows PL spectra of CdTe films obtained with a deep red line (\( \lambda = 752.5 \) nm) of the Kr laser. This wavelength permits one to probe the CdTe at the air interface and at the CdS/CdTe interface through the CdS layer without exciting PL from the CdS. In Fig. 5 we present data from LPVD-fabricated solar cell structures after treatment with CdCl₂ and annealing in air at 400 °C. We find that laser deposited CdTe films grown in a small background pressure of O₂ (0.1 mT) appear to show less interface diffusion as indicated by a smaller shift to longer wavelengths in the PL peak near 790 nm. This shift in the near band edge peak at 80K arises from interdiffusion across the
CdS/CdTe interface producing a region of CdS\textsubscript{x}Te\textsubscript{1-x} alloy with smaller band gap than CdTe. There is some indication that the presence of O\textsubscript{2} during the LPVD growth may inhibit this interdiffusion. Further work is in progress to relate these effects to the cell performance and to examine their effects in sputtered films.

Conclusions

Cells prepared by rf sputtering of both CdS and CdTe have yielded relatively high open circuit voltages (typically 0.80 - 0.82 V) with good uniformity across ~ 3 inch substrates. However, the short-circuit currents are only 17 to 18 mA/cm\textsuperscript{2} mostly due to the relatively thick CdS (0.3 to 0.6 µm). Efforts in the coming year will focus on reducing the optical absorption in the window layer while maintaining high \(V_{oc}\). Other work will seek to improve the diagnostics for monitoring and controlling the reproducibility of the sputter process and to achieve additional control over the electrical properties of the CdTe films and companion materials.

References

Fig. 3. Growth rate of sputtered CdS films vs. gas pressure. $T_s = 325°C; P_{rf} = 120$ W.

Fig. 4. Areal density of grains for post-growth annealing, vs. $1/T$. Straight-line fits yield enthalpy for grain boundary movement.

Fig. 5. 77K photoluminescence with 752 nm excitation from LPVD-grown CdS/CdTe solar cells grown with and without oxygen. Data taken after post-growth CdCl$_2$ treatment and 400°C air anneals. PL excited from CdTe/air interface and CdS/CdTe interface.
OBJECTIVES

The primary objective of this program is to determine if ZnSe is a viable alternative to CdS as a window material for CIS-based and CIGS-based solar cells. A discussion of the technical approach used in these studies follows.

TECHNICAL APPROACH

The program is structured into three tasks: (1) CIS and CIGS cells with ZnSe windows; (2) Material and device characterization; and, (3) Device modeling. Task 1 comprises the major thrust of the program. During FY 93 efforts on this task mainly involved studies of ZnSe/CIS cell structures based on Siemens CIS substrates. ZnSe is grown by MOCVD. An approach to MOCVD deposition of ZnO is still being developed. To date, solar cells have been fabricated by having ZnO deposited at other laboratories, and then depositing a collector grid at WSU. Devices are characterized by carrying out I-V analyses and external photoresponse measurements. Physical characterization involves collaboration with NREL. Device modeling studies involves investigation of current loss mechanisms with emphasis on correlation of device performance with cell processing.

RESULTS FOR FY 93

MOCVD Growth Of ZnSe And ZnO

ZnSe/CIS heterojunctions are fabricated by depositing ZnSe films onto CIS substrates by MOCVD. Growth of ZnSe is accomplished in a SPIRE 500XT reactor housed in the Electronic Materials Laboratory at WSU Tri-Cities by reacting a zinc adduct with H2Se. ZnSe is is doped with iodine using ethyl iodide mixed with helium as a source. Substrate temperatures are typically 250°C. ZnO has also been deposited by MOCVD by reacting tetrahydrofuran (THF) with a zinc adduct. The gas delivery system for ZnO growth had to be repaired as a result of interaction of components with THF. The system is expected to be back in operation early in FY 94.

ZnSe/CIS Test Devices

This work has been conducted using CIS substrates from Siemens Solar. These substrates consist of a CIS layer deposited onto Mo coated glass. Siemens 10 cm square substrates are diced into nominally 2 cm x 2 cm die for various studies discussed below. Al/CIS Schottky barriers have been utilized extensively in this work for diagnostic purposes. For example, Al/CIS barriers were utilized for determining an approach to surface treatment prior to ZnSe deposition to form a heterojunction. It was determined that etching CIS substrates with either KBr,Br or KCN aqueous...
solutions prior to Al deposition leads to consistent Al/CIS Schottky barrier properties. ZnSe/CIS heterojunctions have been studied by growing n-ZnSe films onto 2 cm x 2 cm CIS substrates and then depositing an array of thin, transparent aluminum circular areas 2.8 mm in diameter on top of the ZnSe to serve as contacts. Typically, the Al films are deposited with a thickness of 100 Å to 120 Å so that light can pass through the film, thus allowing illuminated characteristics of the ZnSe/CIS junction to be tested. Figure 1 gives illuminated I-V characteristics for a test device illuminated by an ELH bulb simulator with the intensity adjusted so that J_sc = 40 to 41 mA/cm². The efficiency is designated as the estimated active-area AM1 efficiency. The device structure is also described in Figure 1. It is significant that under conditions for which the photon flux entering the ZnSe/CIS structure is similar to that for AM1 illumination, the open-circuit voltage is 506 mV.

ZnSe/CIS Solar Cells

ZnO/ZnSe/CIS solar cells have been fabricated primarily by having ZnO deposited by Siemens onto ZnSe/CIS structures, and then completing the device at WSU. Collector grids are formed by depositing 100Å to 300Å of Ni onto the ZnO top contact layer followed by several microns of silver. To date, we find that ZnO deposited by the Siemens process causes photocurrent suppression. A typical example of this effect is illustrated by the illuminated I-V characteristics of cell 93ZC417 shown in Figure 2. One possible explanation of this effect is that excess oxygen reacts with ZnSe during the ZnO deposition process. Since excess Se is known to cause deep states in ZnSe, it seems reasonable to expect oxygen to have the same effect. Deep states could cause the ZnSe to become compensated and much more resistive. Preliminary calculations assuming a model based on formation of deep electron traps in ZnSe indicate that such a model can lead to a bias dependent photocurrent effect, and predict illuminated I-V curves as measured for 93ZC417. Characterization of ZnSe layers with photoluminescence and depth concentration profiles with SIMS will be done in the near future to assist us in understanding the cause of the inflected I-V curves. It should also be noted that ZnO deposited onto ZnSe/CIS structures by Boeing (with a RF sputtering process) also resulted in inflected I-V curves.

Based on the hypothesis that the Siemens ZnO deposition process causes a physical change in the ZnSe layers of ZnSe/CIS junctions, solar cells have been fabricated by incorporating a conductive, wide bandgap layer in the cell structure to protect the ZnSe. One convenient approach to depositing such a layer consists of solution growth of another II-VI compound. Since ZnO can be deposited onto solution grown CdS layers without extreme deleterious effects, our initial approach to forming a protective layer has consisted of using solution grown CdS protective layers. If a protective layer is required in the long term, it will be desirable to utilize a non-cadmium film. Illuminated and dark characteristics of a 2.16 cm² cell fabricated with a CdS protective layer are given in Figure 3. The basic approach to incorporating the protective layer in the cell structure is also described in Figure 3. Illuminated characteristics (measured at WSU) are shown together with dark characteristics to clearly demonstrate that the dark I-V curve does not translate into the power quadrant. Thus, even with the protective layer, the CdS solution growth process and/or ZnO deposition procedure has degraded the potential performance of this ZnSe/CIS cell. In particular, the potential performance of this cell based on the dark characteristics is 15 %. The dark characteristics can be interpreted in terms of two current loss mechanisms, one dominant at low voltages (0.1 to 0.3 Volts) and one dominant at high voltages (> 0.4 Volts). The high voltage mechanism is characterized by A = 1.44, and J_0 = 4.8 x 10^-8 A/cm². These I-V parameters are very good for a CIS cell. Clearly, we are motivated to understand the cause of the inflected I-V curves, and therefore, be able to take advantage of the potential of the ZnSe/CIS cell structure.

The cell discussed above was also sent to NREL for characterization. Illuminated characteristics measured by NREL are given in Figure 4. Note that Voc = 509 mV. Although the total area
efficiency is a respectable 9.28 %, significantly higher efficiencies appear possible once the fill factor is increased.

Conclusions

Studies of CIS solar cells based on ZnSe windows indicate that ZnSe may be a viable alternative to CdS. ZnSe window layers are grown by MOCVD, which may explain the relatively large open circuit voltages attained compared to other results reported in the literature. Future investigations will concentrate on understanding the interaction between ZnO deposition processes and ZnSe, which currently is limiting the performance of ZnSe/CIS cells. Once the cause of the inflected I-V curves is understood, ZnSe/CIS solar cells should exhibit efficiencies > 14 %.

Figure 1. Test device structure for ZnSe/CIS cells, and illuminated I-V characteristics of one of the devices on substrate 93ZC424.

Figure 2. Inflected illuminated I-V curve for ZnSe/CIS solar cell with ZnO top contact layer and collector grid.
Figure 3. Dark and illuminated characteristics of a 2.16 cm$^2$ ZnSe/CIS solar cell with a CdS protective layer (Cell 93ZC465). Adjacent figure describes the cell structure incorporating a protective layer.

Sample: 93ZC465
Aug 31, 1993 1:59 PM
Area = 2.157 cm$^2$
Spectrum: ASTM E892-87 Global
Irradiance: 1000.0 Wm$^{-2}$

$V_{max} = 0.3746$ V
$I_{max} = 53.44$ mA
$P_{max} = 20.02$ mW
Efficiency = 9.28%

$V_{oc} = 0.5094$ V
$I_{sc} = 75.88$ mA
$J_{sc} = 35.18$ mAcm$^{-2}$
Fill Factor = 51.79%
Two kelvin probes

Figure 4. Illuminated current-voltage characteristics measured by NREL for ZnSe/CIS cell with a CdS protective layer. Both dark and illuminated characteristics of this cell are given in Figure 4.
4.0 AMORPHOUS SILICON RESEARCH PROJECT

Werner Luft (Manager)

Amorphous silicon (a-Si) PV commercial products had a 26% share of the worldwide PV market in 1992. The product is reliable, as exemplified by 10-year warranties for commercial power modules. The potential for low costs is the same as for any other thin-film PV technology, namely $1-2/W_p. Gradual efficiency improvements are constantly being demonstrated. The best prototype module stable efficiencies are now reported to be 9.5%.

A transition in emphasis did occur in FY 1990 from single-junction a-Si cell and submodule research to multijunction module research, and from initial efficiency to stabilized efficiency. NREL implemented the transition in FY 1991 to focus industrial subcontractors and university subcontractors on stabilized efficiencies, rather than to focus on maximizing initial performance and minimizing degradation. The focus on stabilized efficiency was continued in FY 1993.

The previous 3-year cost-shared subcontracts between industry and government are coming to an end in FY 1994. Likewise, the 3-year fundamental research subcontracts with universities will generally come to an end in the second quarter of FY 1994. Both of these activities will be replaced with one a-Si subcontracted research activity in which both industry and universities will participate. The new 3-year activity will be directly integrated with the a-Si team plans that were developed in FY 1993 in a cooperative effort among NREL, industry, and universities. For that purpose a solicitation for Letters of Interest was issued in April 1993. Awards resulting from that solicitation are expected by mid-FY 1994. Any awards to industry will be cost-shared by industry at a level of at least 50%. In addition to these subcontracts, there is an existing 4-year subcontract on thin films with the Institute of Energy Conversion (IEC) at the University of Delaware.

Some other FWPs support the Amorphous Silicon Research Project: PV Manufacturing Technology (PVMaT) Project for cost reductions of modules, and the Module and Systems Performance and Engineering Project for reliability and performance testing of modules. Coordination among the various projects enhances the probability of success of the a-Si technology in the marketplace.
OBJECTIVES

The objectives of the a-Si research project are to 1) develop a cost-effective a-Si PV technology to foster a viable a-Si PV industry in the United States, ensuring that this industry remains a world leader in the a-Si technology; 2) help the U.S. a-Si PV industry achieve the U.S./DOE PV Program FY 1995 milestone of 10% stable efficiency commercial thin-film modules; 3) help the U.S. a-Si PV industry to achieve 12% stable efficiency commercial thin-film modules by 1998; and 4) achieve 15% stable efficiency multijunction a-Si:H modules for large-scale electric utility use by the year 2005.

The first objective, to reduce the costs to $1/W_p, and to foster a viable a-Si PV industry in the U.S., is partially pursued via the PVMaT project and partially via the a-Si research project in that higher stable efficiencies translate into lower cost.

The second objective is addressed by the research team formation described below.

The third objective, to achieve 12% stable prototype module efficiency by 1998, will be pursued through better understanding and improvement of the optoelectronic properties of a-Si-based alloy materials. This objective requires a better understanding of the metastability in a-Si.

The fourth objective, to achieve a-Si module stable efficiencies of 15%, together with elimination of the Staebler-Wronski effect, reduction of module costs for electric utility bulk-power applications to $0.50/W_p (or $50/m^2), corresponding to 6 cents/kWh, will be attacked through mission-oriented university and NREL research in close cooperation with the a-Si PV industry.

APPROACH

To achieve the objectives in a timely and efficient manner, NREL established four a-Si; research teams in November 1992: a Wide-Bandgap Alloy Team, a Metastability and Mid-Bandgap Alloy Team, a Low-Bandgap Alloy Team, and a Device Design and Interfaces Team. These teams consist of researchers in industry, at universities, and at NREL. The organizations presently represented on the four teams are as follows:

Wide-Bandgap Alloy Team:
U. Illinois, Penn State U., U. Syracuse, Xerox, NREL

Metastability and Mid-Bandgap Alloy Team:

Low-Bandgap Alloy Team:
U. Oregon, Iowa State U., Institute of Energy Conversion, North Carolina State U., Colorado School of Mines, NREL,
Industry: Solarex, USSC, Energy Conversion Devices
We expect that well coordinated team efforts with well-defined mission objectives will lead to more rapid progress toward the 15% efficiency goal for the year 2005 than a diffused effort by many independent researchers. Having agreed on a triple-junction structure, the researchers determined the stable characteristics that must be achieved for the three subcells in the structure and for the combined structure to reach the stable efficiency goal of 15%. These parameters are shown in Table 1. These parameters are applicable to a multibandgap structure with the bandgaps for the components as indicated in the Table. The goal may change if the bandgap distribution between the subcells is changed. The present status of corresponding parameters for small a-Si cells is shown in parentheses in Table 1 and is based on data from the PV industry. The mid- and low-bandgap small cells were degraded under 1000 W/m² illumination with filters. All cells were light soaked for 600 hours at 50°C.

Table 1. Long-term a-Si module stabilized performance goals

<table>
<thead>
<tr>
<th>Team</th>
<th>Bandgap (eV)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>Jsc (mA/cm²)</th>
<th>Power (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wide-Bandgap†</td>
<td>1.9-2.0</td>
<td>1.10 (0.98) d)</td>
<td>0.75 (0.68) d)</td>
<td>&gt;8.0 (8.0) d)</td>
<td>&gt;6.6 (5.3) d)</td>
</tr>
<tr>
<td>Mid-Bandgap(a)†</td>
<td>1.70-1.75</td>
<td>0.95 (0.87) c)</td>
<td>0.75 (0.61) c)</td>
<td>&gt;8.4 (6.2) c)</td>
<td>6.0 (3.3) c)</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>1.60-1.65</td>
<td>0.89 (0.74) c)</td>
<td>0.70 (0.57) c)</td>
<td>8.4 (6.8) c)</td>
<td>5.2 (2.9) c)</td>
</tr>
<tr>
<td>Low-Bandgap(b)</td>
<td>1.40-1.45</td>
<td>0.68 (0.65) c)</td>
<td>0.68 (0.56) c)</td>
<td>&gt;8.6 (7.7) c)</td>
<td>&gt;4.0 (2.8) c)</td>
</tr>
<tr>
<td>Devices</td>
<td>2.67 (2.44)‡</td>
<td>0.72 (0.61)‡</td>
<td>&gt;8.0 (7.7)‡</td>
<td>15 (11.5)‡</td>
<td></td>
</tr>
</tbody>
</table>

(a) under λ>530 nm light as seen by the mid-cell in a triple-stack
(b) under λ>610 nm light as seen by the bottom-cell in a triple-stack
(c) United Solar Systems Corporation data
(d) Solarex Corporation data
† with Cr reflector for low reflectance. ‡ 360 hours light soaking

The best stabilized module (approximately 0.09 m² size) efficiencies as measured under a solar simulator that have been reported are given in Table 2.
Table 2. Best a-Si module stabilized efficiencies (measured with a solar simulator after 600-1000 hours of light soaking)

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Module Type</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solarex</td>
<td>Si/Si/SiGe</td>
<td>8.8†</td>
</tr>
<tr>
<td>USSC</td>
<td>Si/Si</td>
<td>6.2‡</td>
</tr>
<tr>
<td>USSC</td>
<td>Si/SiGe</td>
<td>9.5†</td>
</tr>
<tr>
<td>USSC</td>
<td>Si/Si/SiGe</td>
<td>9.4†</td>
</tr>
<tr>
<td>Energy Conv. Devices</td>
<td>Si/Si/SiGe</td>
<td>7.8 (0.39 m²)</td>
</tr>
<tr>
<td>Fuji</td>
<td>Si/Si</td>
<td>9.0</td>
</tr>
<tr>
<td>Advanced PV Systems</td>
<td>Si/Si</td>
<td>6.0†</td>
</tr>
</tbody>
</table>

† Not verified by NREL measurements, ‡ Commercial 0.36 m²

Each of the four teams is addressing a number of research issues that have been identified by the researchers to be essential to meet the long-term objectives. The individual teams have defined the problems that must be overcome to achieve the parameters indicated in Table 1, defined the root causes for the problems, and the countermeasures to be taken.
Title: Defect Spectroscopy on amorphous silicon devices

Organization: NREL, Golden, Colorado

Contributors: R. S. Crandall, principal investigator

Objective: To determine why some a-Si:H and a-SiGe:H solar cells degrade during illumination at different rates and to a different degree than films. To develop new solar cell diagnostic methods. To gain a better understanding of the important cell degradation mechanism. To determine what film properties are good predictors of cell behavior. To measure the barrier height between the ZnO/p-a-Si:H interface in order to reduce this barrier to negligible levels for PV operation.

Approach: There is increasing evidence that films and solar cells made under similar conditions degrade differently. There are reports that some material exhibits little increase in midgap-defect density or reduction of photoconductivity and diffusion length. Nevertheless, p-i-n solar cells made using i layers of material similar to that in the film often show significant degradation. In other cases films and solar cells degrade in a similar manner. The cell degradation can be modeled for the later example with the increase in midgap defects (recombination centers) observed in the corresponding film. To attempt to clarify this situation, we are applying Admittance Spectroscopy techniques to measure defects in solar cells. The results that can then be used to compare with film degradation and more importantly as input to solar cell modeling.

Results: Various admittance techniques were used to study the defects in solar cells. However, the most reliable information was obtained using Drive-Level Capacitance profiling. This technique permits one to determine the density and spatial location of deep defects in the i-layer of a p-i-n cell at different stages of solar cell degradation. An example of the application of this technique is shown in Fig. 1. The data show the defect density as a function of depletion width, =ε/C , where ε is the dielectric constant and C the capacitance per unit area. The i layer of the p-i-n device is 1.2µm thick. The data show the following salient features. Light soaking increases the defects in the central region of the device, rather than near the interfaces. The defects decrease dramatically away from the p-i-n interface attaining their minimum value near the middle of the i-layer. Although not shown here, the defect density increases abruptly at the n-i interface. We believe that these interfacial defects are thermodynamic in origin. Evidence of this is shown by the data points in the figure obtained from a published solar cell simulation. This simulation included the effects of defects near the interface that are produced as a result of applying equilibrium thermodynamics.

Future Direction: These and similar measurement of defect density will be made during the next Fiscal year with emphasis on using the results as input for solar cell simulation using the AMPS model. Measurements on p-i-n cells with different alloys of amorphous silicon will also be made. The results will also be used as a guide to change deposition conditions to reduce these defects.
Figure 1. Defect density in units of $1 \times 10^{16}$ cm$^{-3}$ versus depletion width in the annealed and light soaked under AM1 conditions for 15hr.

References:
Experimental Investigations of Metastability Mechanisms in a-Si:H

PRINCIPAL INVESTIGATOR: Howard M. Branz, NREL, Golden CO

CONTRIBUTORS: Howard Branz, Eugene Iwaniczko, Brent Nelson, Sally Asher

OBJECTIVE:
To test experimentally the role of H in the Staebler-Wronski effect in hydrogenated amorphous silicon (a-Si:H).

TECHNICAL APPROACH:
We examined the roles of hydrogen and hydrogen motion in metastability in hydrogenated amorphous silicon. We studied light-enhanced diffusion of H at different temperatures to understand the nature of carrier-induced H release and capture. We studied applicability of the hydrogen glass model of metastability by quenched-in conductivity and H diffusion measurements on P-doped a-Si samples with different H contents.

LIGHT-ENHANCED DIFFUSION:
Figure 1 shows D depth profiles of an a-Si:H/a-Si:H:D/a-Si:H sandwich sample taken after 2 days anneal at 240°C. The results are from three different regions of a single unbroken sample. As indicated in the figure legend, these regions were Al-foil shadowed, black-graphite-paint shadowed and white-light illuminated. The Al-foil and black-paint shadowing yield identical profiles, but the light enhancement of diffusion is easily observed in the unshadowed portion.

This experiment demonstrates that the light-enhanced D diffusion is not a thermal effect. Although the film under the black paint is heated more than the illuminated portion, light enhancement is observed only where light enters the a-Si:H. The Al-foil and black paint regions yield indistinguishable profiles despite their different values of reflectance. We conclude that the light-enhancement effect is caused either by the light itself or by light-generated carriers. The intensity and temperature dependence of the light-enhancement [1] suggest that the light-generated carriers cause the effect.

Figure 2 shows the D profile after dark and illuminated 12-hr anneals at 210°C. The dark anneal profile is in the "early-time" regime [2] and the exponential wing decay length yields a mean displacement before retrapping of \( \lambda = 115 \pm 30 \) Å and an H release time of \( \tau = 60 \pm 20 \) hrs. Illumination changes both \( \lambda \) and \( \tau \). The shape of the curve becomes characteristic of the intermediate-time regime, and \( \tau \sim t = 12 \) hrs. In the intermediate-time regime, the measured decay length of the wing, \( 75 \pm 30 \) Å, represents an upper limit to \( \lambda \). We estimate that the actual value of \( \lambda \) is about 50Å. Evidently, illumination increases the H detrapping rate (decreases \( \tau \)) and decreases the mean D displacement before retrapping.

The relationship between light-enhanced Si-H bond breaking and light-induced metastability at room temperature remains uncertain. We do not observe any light-enhanced diffusion effects below 210°C. However, \( D_H \) extrapolates to such a low value at room temperature that we would not expect to observe either light-induced bond-breaking or diffusion. The existence of light-enhanced diffusion at higher temperatures does supply a plausible intermediate step to H models of the Staebler-Wronski effect in a-Si:H.

HYDROGEN GLASS MODEL:
Street et al. [3] postulated a 'hydrogen glass' model of metastability in which H diffusion mediates defect creation and annealing in a-Si:H. We have obtained new evidence that this H-glass model of metastability is applicable to quenched-in metastability in P-doped a-Si:H. [4] We observe quenched-in metastability of the dark conductivity in P-doped a-Si containing only 0.1 at.% of H (Sample LH), with an annealing temperature of \( T^* = 355 \pm 20 \)°C. This is more than 200°C higher than \( T^* \) found in P-doped glow-discharge (GD) a-Si:H containing 10 at.% H. After we hydrogenated this a-Si sample with 10 at.% of H (Sample HH), \( T^* \) fell to 175° ± 20°C, closer
to the glow-discharge value. Measured values of hydrogen concentration (C_H) and of D_H at T* are given in Table I.

To interpret our data, we derived a quantitative prediction of the H-glass model: the H diffusion coefficient at T*, D_H(T*), should be inversely proportional to the H concentration. As indicated in Table I, our measurements and published data for P-doped GD a-Si:H agree with this prediction. The H glass model describes our data for P-doped films. However, previously published data for metastability annealing and H diffusion in undoped a-Si:H suggest there may be no connection between H diffusion and metastability annealing in undoped a-Si:H. More research is needed to settle this important issue.

REFERENCES:


FIGURES AND TABLE:

Figure 1. SIMS profiles of D after 2 days annealing at 240°C. Illumination and shadowing techniques are indicated in the legend.
Figure 2. D profiles after 210°C anneals for 12-hrs in the dark and under illumination. An as-grown profile is also shown.

Table 1. Measured values of H-glass model parameters in P-doped amorphous silicon.
The aim of this research is to establish and understand the Hot Wire (HW) deposition technique, and the material properties for a-Si:H and a-SiGe:H materials suitable for stable high efficiency solar cells. Because of the temporary shutdown of deposition facilities due to safety considerations involving the use of concentrated silane, we were not able to perform those material and film characterizations which required the need to deposit HW films on specialized substrates, such as those needed for SAXS, H evolution and NMR studies. However, we were able to study the H bonding of the HW films from an IR standpoint, and were also able, in this interim period, to demonstrate the deposition of HW device quality a-Si:H using a "safe" gas source, one which does not require the stringent safety controls usually associated with the use of concentrated silane. Regarding the first investigation, we studied and presented results on H diffusion on GD and HW films by a new technique (1). In this technique, a-Si:H films deposited on crystalline silicon were isochronally annealed for fixed times, and after each anneal the decrease in the amount of SiH absorption was carefully measured by IR. These data were then incorporated into the rate equation for loss of SiH bonds due to annealing, enabling the determination of an activation energy to break these bonds and put the H into sites that cannot be measured by IR. The activation energies so obtained for GD films were quite similar to the H diffusion energies found in the literature, suggesting that diffusion parameters could be obtained by this method. On the other hand, a similar analysis for HW films was not as conclusive. In particular, the rate of HW SiH bond breaking was observed to occur faster than for GD films containing similar H contents. Since one possibility to explain this relatively fast behavior is that of H effusion through microvoids, structural experiments (H evolution, SAXS) need to be performed on these HW samples to enable an understanding of this HW SiH loss process. In the second investigation, we not only deposited, for the first time, device quality a-Si:H samples with a "safe" gas source, but fully characterized the electronic and structural properties of these films as well. In particular, the film deposition rates were found to be comparable to these of GD samples (1-2Å/s), and the ambipolar diffusion lengths of 1700-1800Å were better than the best GD values. At this point, these films typically contain about 10 at.% H, and an investigation is underway to see if the H contents can be lowered with a preservation of device quality electronic properties, as we were able to do with HW samples deposited with concentrated silane. Further, an examination of the film electronic properties as a function of deposition chamber pressure and/or filament to substrate spacing has pointed out the necessity of gas phase reactions to enable deposition of device quality material.

Title: Deposition of PECVD and Hot-Wire a-Si:H Materials and Devices using Pure Silane

Organization: NREL, Golden, Colorado

Principal Investigator: Brent P. Nelson

Objective

Continued support of the internal amorphous silicon (a-Si:H) group and the external a-Si:H community, by way of supplying state-of-the-art a-Si:H films and devices. Make a-Si:H solar cells with increased stabilized performance using the hot-wire (HW) deposition technique to deposit one or more of the layers.

Approach

The conventional, and by far most commonly used, deposition technique to produce a-Si:H solar cells is Plasma Enhanced Chemical Vapor Deposition (PECVD) using concentrated silane as the primary gas source. During this performance period we relocated two deposition systems with PECVD capabilities to the Amorphous Silicon Deposition Laboratory (ASDL) in NREL's Joyce Street Facility (JSF). This facility meets or exceeds all of the codes and safety requirements for the safe use of pure silane and the other process gases we use. Both systems (described in the following section) in the ASDL are fully operational. Before we could operate either system, they each had to pass a thorough and exacting Operational Readiness Review; verifying the safety of the systems relative to a 25 page checklist.

Research Results (expected FY 93 milestones in italics)

Make fully operational the "S" system. -- The Single Chamber Amorphous Silicon Deposition System ("S" System) is fully operational. It utilizes a single, 4.5" conflat, 6-way cube as the deposition chamber. Its design and current configuration is solely for PECVD of a-Si:H and a-Si:H alloys. There are eight separate gas lines going to this system: pure silane; ppm level diborane in silane; phosphine in helium; trimethylboron in helium; germane in helium; methane; hydrogen; and deuterium. The use of a load lock enables us to load and unload substrates from the deposition chamber without exposing it to atmosphere.

Make fully operational the "T" system. -- The Two Chamber Amorphous Silicon Deposition System ("T" System) is fully operational. It utilizes two separate, 6.75" conflat, 6-way crosses as the deposition chambers. We deposit doped layers (p- and n-layers) in one chamber and intrinsic layers in the other chamber. Samples are moved back and forth between the two chambers through the load lock. This enables us to keep the samples under vacuum between the various layers in a solar cell. See the figure on the following page for a top view of the "T" System.

The design of the "T" System is more flexible than that of the "S" System because both chambers are readily changeable between PECVD, Hot-Wire, or even Remote Plasma technologies. The current configuration of the system is to make p- and n- layers by PECVD and the i-layer by Hot-Wire. There are also eight separate gas lines going to this system: two pure silane lines (one for each of the two chambers); diborane in helium; phosphine in helium; germane in helium; methane; hydrogen; and deuterium.

Deposition and comparison of hybrid Hot-Wire/PECVD to all-PECVD solar cell devices. -- We were able to quickly obtain positive results for our all PECVD solar cells. Once we made a few devices with conversion efficiencies close to 10% (Voc = 0.78 Volts, Jsc = 18.36 mA/cm², ff =
0.68, efficiency = 9.7% -- typical), we began to look at p-i-n devices that have i-layers made using the Hot-Wire technique. Using the same recipe as the all PECVD devices, we were able to make such a hybrid solar cell with a conversion efficiency of 7% (Voc = 0.80 Volts, Jsc = 15.3 mA/cm², and ff = 0.60). However, due to problems with our top metal contacts we have not been able to compare the stabilized efficiency of these hybrid devices to our all PECVD devices. The ability to make hybrid cells in the same system that is capable of making all PECVD devices is both unique and significant, because it allows us to "compare apples to apples."

Future Research

We will continue to improve the conversion efficiency of hybrid Hot-Wire/PECVD solar cells. We will initiate a comprehensive comparison of the stabilized efficiency of hybrid cells to all PECVD cells. Finally, we will continue to support the internal amorphous silicon group and the external a-Si:H community, by way of supplying state-of-the-art a-Si:H, and a-Si:H alloy (a-SiC:H and a-SiGe:H) films and devices.
Objective a: To find the source of and understand the mechanism by which shunts cause additional light-induced degradation in multi-junction a-Si:H cells. To understand why these shunts anneal at 150°C.

Approach: Shunt conductance associated with a point source usually exhibit a microplasma type of punch-through behavior. The effect on the shunt current would be to cause large current fluctuations as these current spikes turn on and then quench. We will be looking to verify this kind of current noise behavior.

It is quite possible that the shunts that turn on with light do not penetrate all three of the layers of the triple cells in the annealed state. When HeNe laser light illuminates a triple junction cell, the photo current produced in the front cell is less than 1/3 the current produced in the middle or back cells. When measuring the light I-V characteristic, the front cell will become reverse biased before either of the two back cells. If none of the cells is shunted, the light I-V characteristic will be current limited by the front cell. If the top cell is shunted, its photo current no longer limits the current that is produced by the back cells as it is forced into reverse bias.

Studying such a light I-V characteristic can tell whether or not the current limiting junction is shunted.

Multi-junction P-I-N cells from Solarex and other manufacturers will be the first cells studied.

Results: It is widely believed that the light-induced degradation phenomenon associated with hydrogenated amorphous silicon (a-Si:H) can be circumvented with the use of thin, tandem p-i-n cells. However, when a textured CTO-glass substrate is used for either thin single p-i-n or thin multilayer p-i-n structures, a new mode of cell degradation occurs which has been associated with the increased shunting. Physical shunts that contribute to an increased shunt conductance in the dark and the voltage-dependent carrier collection efficiency that determines the slope of the light I-V through zero-bias, are entirely different physical quantities. In cells with a moderate initial shunting, light-induced degradation of the slope in the light I-V through zero-bias will be enhanced as a direct result of an increase in shunt conductance.

In a collaboration with Solarex, Corp. triple-junction cells were examined before and after light-soaking using dark I-V analysis. It is clear that two degradation mechanisms are occurring: i) The classical bulk Staebler-Wronski 3 defect generation mechanism causes an increase in diode quality factor in cells that show very little shunting in the forward and reverse I-V characteristics. ii) In the cells exhibiting more as-grown shunting behavior, white light illumination introduces enhanced shunting degradation. When measuring the reverse current at -0.1V, incremental current steps of 5-20 nA are observed to switch on and off in the shunted diodes. New shunts can be introduced with forward bias and eliminated with reverse bias. The behavior of these fluctuations is very similar to the switching mechanism found by LeComber et al. We think this new mode of cell degradation is caused by an increase in the number of shunt pathways and not by enhancing current through existing shunts. Shunting varies regionally with mm spatial distances and is not correlated with any visual features.

Measurements on several triple (thin cell on the CTO) and a double (thick cell on the CTO) junction cells have been compared. The data show that i) the top, current-limiting cell is shunted only when in contact with the textured CTO, ii) shunting is initially limited to one layer of a multijunction cell, and iii) the top cell can be shunted to the same extent in triples that are shunted and triples that are not shunted. Ongoing work will include examination of doubles and finally triples with i) the thin, frontcell deposited first on the CTO and the configuration with ii) the thick, backcell deposited first on the CTO. The understanding how shorts form in the triple cell and how light-induced shunting can occur can proceed by examining HeNe I-V curves of these devices.
Objective b: To compare the fairly well understood dangling bond in porous silicon (PS) to the dangling bond in hydrogenated amorphous Si (a-Si:H) films. Look for evidence of light-induced metastability on a H-passivated PS film.

Approach: We compare the electron spin resonance (ESR) signal of the dangling bond in porous silicon (PS) layers, produced by electrochemical etching, to the ESR signal from hydrogenated amorphous Si (a-Si:H) films. We will look for light-induced metastability on a H-passivated PS film.

Results: The anisotropy of the ESR signal from PS showed g values varying as for the Pb Si/SiO₂ interface dangling bond.⁶ The g value varies from $g_\parallel = 2.0020$ to $g_\perp = 2.0080$ with an inhomogeneously broadened line width increasing from 1.8 to 3.8 G. An ESR powder line, with superhyperfine and strain broadening intrinsic to PS, has more anisotropy in $g_\parallel - g_\perp$ and less inhomogeneous broadening than does the dangling bond line in a-Si:H.

The difference in the ESR line shapes on these two materials occurs because the defect is formed quite differently in each film. In PS, the crystal is whole and dangling bonds are formed as material is removed. On the other hand, in a-Si:H the material is being grown far from equilibrium. A dangling bond is formed when the topological disorder is so bad that it becomes more favorable, from the standpoint of reducing the total energy, to form a dangling bond than to increase the stress any further in local bonds by requiring four-fold coordination. As a result, back bond angle variations will be larger in a-Si:H and X-ray data confirm this.⁷ Our ESR results agree, showing a larger inhomogeneous line broadening in both W_∥ and W_L for the a-Si:H than for the PS powder.

The smaller anisotropy in $g_\parallel - g_\perp$ for the dangling bond in a-Si:H is evidence for less anisotropy in the crystalline fields next to the dangling bond in a-Si:H than next to the dangling bond in PS. The process of incorporating a dangling bond in a growing disordered material produces a more isotropic local environment than the process of stripping away material to produce a dangling bond in an ordered crystal.

Finally, on a H-passivated PS film used in an earlier study⁸ we find no evidence of light-induced metastability. The number of spins was unchanged after white light exposure for 1 day and then again after annealing at 150°C. Possibly, this negative finding is because a more ordered/rigid structure cannot undergo the structural relaxation required to stabilize a dangling bond.

References

Research on Stable, High-Efficiency Amorphous Silicon
Multijunction Modules
Phase II

Advanced Photovoltaic Systems
Princeton, New Jersey

F.J. Kampas, program manager
M. Ghosh and J. Xi, principal investigators

Objectives

The overall goal for this research program is the demonstration of a stable, aperture area efficiency of 10% for two-terminal, similar bandgap, multijunction all-amorphous-silicon-alloy modules having an aperture area of at least 900 cm$^2$. The major milestones for Phase II of the program are demonstration of an amorphous silicon, similar-bandgap multijunction module with a stable aperture-area efficiency greater than 8% and a 1 cm$^2$ multijunction cell with a stable efficiency greater than 9%.

Approach

Two groups in APS' R&D department worked on the project: the Device Group and the Module Group. The Device Group concentrated on developing improved tandem junction structures and component layers of those structures. This work was performed by producing 1 cm$^2$ diagnostic layers and devices in two small-area deposition systems which utilize 5 cm x 5 cm substrates. Results of this research were then transferred to the Module Group for scale up to 900 cm$^2$ modules. The Module Group also made diagnostic 1 cm$^2$ devices on 900 cm$^2$ substrates for purposes of layer and structure optimization. Reoptimization of layer deposition conditions is required when structures are transferred from the small area to the larger area deposition systems, due to the different electron energy distributions in the different deposition systems, which results in different layer compositions for the same gas mixtures.

One research issue occupied the majority of the investigative effort. This was the development of a good "tunnel junction" structure between the two p-i-n structures of the tandem. The "tunnel junction" between the two p-i-n structures is the site of recombination between the electrons from the n-layer of the first p-i-n structure (n1 layer) and holes from the p layer of the second p-i-n structure (p2). In crystalline semiconductor tandems, electrons tunnel directly from the conduction band of n1 to the valence band of p2. However, the mechanism in amorphous semiconductor tandems is not well understood. This lack of basic understanding makes device optimization more difficult.

Device Results

Good results were obtained by the Device Group for two different tandem structures, with different tunnel junctions. The simpler of the two structures was Asahi "U" tin oxide/ZnO/p1+/p1/b1/i1/μc-n1/p2+/p2/b2/i2/n2/ZnO/Al. The tunnel junction structure is shown in bold letters. The "b" layers
are buffer layers between the p and i layers. The "p" layers are thin (5 Angstrom thick) p layers with no carbon. The best 1-cm² device with this structure came from run B-765 and had an initial efficiency of 9.32% and an efficiency of 7.47% after 600 hours of light soaking.

Table 1. Selected 1 cm² device results.

<table>
<thead>
<tr>
<th>hours of light soaking</th>
<th>$V_{oc}$ (Volts)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>Fill Factor</th>
<th>Efficiency (%)</th>
<th>Series Resistance (ohm-cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2-240-RWM: Asahi &quot;C&quot; tin oxide/p1/b1/i1/µc-n1/p2/i2/n2/ZnO/Al</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.599</td>
<td>7.79</td>
<td>0.690</td>
<td>8.60</td>
<td>14.8</td>
</tr>
<tr>
<td>600</td>
<td>1.554</td>
<td>7.56</td>
<td>0.635</td>
<td>7.47</td>
<td>27.4</td>
</tr>
<tr>
<td>B-765: Asahi &quot;U&quot; tin oxide/ZnO/p1⁺/p1/b1/i1/µc-n1/p2⁺/p2/b2/i2/µc-n2/ZnO/Ag/ZnO/Al</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.652</td>
<td>7.87</td>
<td>0.717</td>
<td>9.32</td>
<td>24.3</td>
</tr>
<tr>
<td>600</td>
<td>1.58</td>
<td>7.83</td>
<td>0.604</td>
<td>7.47</td>
<td>38.3</td>
</tr>
<tr>
<td>B-720: Asahi &quot;U&quot; tin oxide/ZnO/p1⁺/p1/b1/i1/a-n1/µc-p/p2⁺/p2/b2/i2/µc-n2/ZnO/Al</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.648</td>
<td>8.44</td>
<td>0.691</td>
<td>9.62</td>
<td>27.8</td>
</tr>
<tr>
<td>600</td>
<td>1.624</td>
<td>8.19</td>
<td>0.591</td>
<td>7.85</td>
<td>47.0</td>
</tr>
</tbody>
</table>

The second structure was the same as the first, except for the tunnel junction, which was a-n1/µc-p/p2⁺/p2. The best 1-cm² device with this structure came from run B-720 and had an initial efficiency of 9.62% and an efficiency of 7.85% after 600 hours of light soaking. The addition of an anti-reflection coating on the front surface of the glass raised the stabilized efficiency to 8.1%. Other tunnel junction structures gave poorer results.

The best diagnostic 1-cm² device produced by the Module Group on a 900 cm² substrate (from run D2-240-RWM) had the simpler structure Asahi "C" tin oxide/p1/b1/i1/µc-n1/p2/i2/n2/ZnO/Al. Its initial efficiency was 8.60% and its stabilized efficiency was 7.47%. The initial and stabilized parameters of the three devices are given in Table 1.

Stabilized efficiencies for different tunnel junction structures made in a systematic study are shown in Table 2. The large gain in stabilized efficiency resulting from the use of a microcrystalline doped layer in the tunnel junction is clear from these results. The very large drop in fill factor on light soaking (from 0.691 to 0.494) for the device without a microcrystalline layer of either sort in the tunnel junction is the main factor responsible for this. Previously, devices made without microcrystalline layers in the tunnel junction showed smaller decreases in fill factor on light soaking. This large drop may have resulted because the structure was optimized for a microcrystalline layer.
Table 2. Initial and Stabilized Parameters for otherwise-identical devices with an
\( n_1 / (\mu \text{xtal-p}) / p^+ / p_2 \) tunnel junction

<table>
<thead>
<tr>
<th>Initial</th>
<th>Stabilized</th>
<th>Amorphous n1 layer</th>
<th>Microcrystalline n1 layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{oc} ) (Volts)</td>
<td>( V_{oc} ) (Volts)</td>
<td>1.652</td>
<td>1.580</td>
</tr>
<tr>
<td>( J_{sc} ) (mA/cm(^2))</td>
<td>( J_{sc} ) (mA/cm(^2))</td>
<td>7.87</td>
<td>7.83</td>
</tr>
<tr>
<td>Fill Factor</td>
<td>Fill Factor</td>
<td>0.717</td>
<td>0.604</td>
</tr>
<tr>
<td>Eff. (%)</td>
<td>Eff. (%)</td>
<td>9.32%</td>
<td>7.47%</td>
</tr>
<tr>
<td>no microcrystalline p layer</td>
<td>1.573</td>
<td>1.525</td>
<td>1.648</td>
</tr>
<tr>
<td>7.75</td>
<td>7.49</td>
<td>8.44</td>
<td>8.19</td>
</tr>
<tr>
<td>0.691</td>
<td>0.494</td>
<td>0.691</td>
<td>0.591</td>
</tr>
<tr>
<td>8.43%</td>
<td>5.64%</td>
<td>9.62%</td>
<td>7.85%</td>
</tr>
</tbody>
</table>

Optimization experiments on devices with the a-n1/µc-p/p2+/p2 structure revealed that the stabilized efficiency is very sensitive to the thicknesses of the µc-p and p2 layers. The best results were obtained with µc-p layers about 5 Angstroms in thickness and p2 layers about 85 Angstroms in thickness. Increasing the thickness of the µc-p layer degraded the tunnel junction properties, as indicated by a rapid increase in series resistance. Increasing the thickness of the p2 layer resulted in a decrease in initial and stabilized efficiency. The loss in current from the greater thickness outweighed the gain in voltage before light soaking. After light soaking, a thicker p2 layer gave less voltage, probably also due to degradation of the tunnel junction properties.

Module Results

Due to our limited supply of Asahi tin oxide coated glass, the best tandem modules were fabricated with LOF Tec 10 tin oxide coated glass. The Tec 10 glass has only about 5% haze, which resulted in a low value for current. The initial and stabilized parameters for the best module are given in Table 3. The current density and efficiency are aperture area values. The device structure is the same as given in Table 1 for device D2-240. The higher haze LOF Tec 8 tin oxide coated glass gave higher currents but lower voltages, resulting in lower power output. This loss in voltage is believed to be due to the surface morphology of the Tec 8 glass.

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Table 3. Initial and light-soaked parameters of module D2-211

<table>
<thead>
<tr>
<th>hours of light soaking</th>
<th>$V_{oc}$ / cell Volts</th>
<th>$J_{sc}$ mA/cm²</th>
<th>Fill Factor</th>
<th>Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.622</td>
<td>6.30</td>
<td>0.669</td>
<td>6.84</td>
</tr>
<tr>
<td>600</td>
<td>1.612</td>
<td>6.27</td>
<td>0.593</td>
<td>5.99</td>
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</tbody>
</table>

Results on a diagnostic cell from a 900 cm² LOF Tec 10 substrate also prepared in run D2-211 are given in Table 4, for purposes of comparison with the results in Table 1 for run D2-240, deposited on an Asahi substrate. As expected, the most obvious difference is the 15% greater current resulting from the use of the higher haze Asahi substrate. The Asahi tin oxide coated glass also enabled the attainment of a higher open-circuit voltage.

Table 4. Initial and light-soaked parameters for a diagnostic 1 cm² device from D2-211

<table>
<thead>
<tr>
<th>hours of light soaking</th>
<th>$V_{oc}$ Volts</th>
<th>$J_{sc}$ mA/cm²</th>
<th>Fill Factor</th>
<th>Efficiency %</th>
<th>Series Resistance ohm-cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.568</td>
<td>6.87</td>
<td>0.683</td>
<td>7.35</td>
<td>37.2</td>
</tr>
<tr>
<td>600</td>
<td>1.581</td>
<td>6.56</td>
<td>0.593</td>
<td>6.15</td>
<td>40.9</td>
</tr>
</tbody>
</table>

Substantially better module results are expected in the future, as we have been able to obtain a source of high haze tin oxide coated glass with good surface morphology. Also, the tunnel junction structure with the microcrystalline p layer will be transferred from small area devices to modules.
Introduction

Amorphous silicon based multijunction devices offer the potential for low-cost and high performance modules. In the tandem or triple junction approach, the bandgap and thickness of the i-layer's of each component cell can be optimized to respond to different parts of the solar spectrum resulting in component cells with thinner i-layers and better stability. The objective of this three year cost-shared program is to demonstrate a 12% efficient (FY 1993) stable* module. Towards this goal we have addressed the important technological issues under three separate tasks. These tasks are: (I) semiconductor materials research, (II) non-semiconductor materials research, and (III) module research.

Major accomplishments within these tasks are:

- Improvements in a-Si:H material properties which have led to the demonstration of single junction cells with $V_{oc} > 1.0$ V. Devices with $V_{oc} = 0.95$ V have shown degradation as low as 7.5%.

- Improvements in a-SiC:H material properties which have led to the demonstration of single junction cells with $V_{oc}$ as high as 1.04 volts and degradation as low as 13%.

- The development and scale-up of 'thin' microcrystalline n-layers for the 'recombination junctions' in multijunction devices and modules.

- The demonstration of a-Si/a-SiGe tandem junction devices with initial efficiency as high as 11.1% and stabilized efficiency as high as 9.1%.

- The demonstration of a-Si/a-SiGe tandem junction modules with initial efficiency as high as 10.5% and stabilized efficiency as high as 8.9%.

- The demonstration of a-Si/a-Si/a-SiGe triple junction modules with initial efficiency as high as 11.35% and stabilized efficiency of 8.8%.

* 600 hrs., AM1.5 exposure, 50°C; area ≥ 900 cm²
Task I: Semiconductor Material Research

Amorphous silicon deposited at lower than normal temperature from silane + hydrogen feedstock have significantly better properties than those prepared by pure silane. In devices the improved intrinsic layer results in: (a) higher open-circuit voltage and (b) significantly improved stability against light-induced degradation. Optimization of deposition parameters have resulted in a single junction device with $V_{oc} = 1.023$ V. The J-V characteristics of this device is shown in Figure 1 and Figure 2 shows improvement in stability of thin p-i-n devices where the normalized efficiency versus light-soaking time of a device with initial $V_{oc} = 0.89$ V (low temperature, H-dilution) and an optimized device with initial $V_{oc} = 0.95$ V have been plotted. The degradation has improved from $-11\%$ to $-7.5\%$ even with a higher open-circuit voltage. We have developed and scaled-up very thin (~100A) microcrystalline n-layers for use at the 'recombination or tunnel junction(s)' in multijunction devices and modules. This has resulted in improvements in the $V_{oc}$, the F.F and the current collected in the back junction of multijunction devices. Figure 3 shows the effect of microcrystalline n-layer at the tunnel junction of an a-Si/a-Si tandem junction device.

![Figure 1](image1.png)  
**Figure 1** J-V characteristics of an a-Si:H single junction solar cell with $V_{oc} > 1.0$ V.

![Figure 2](image2.png)  
**Figure 2** Stability improvements in thin a-Si:H single junction cells.

![Figure 3](image3.png)  
**Figure 3** J-V characteristics of two a-Si/a-Si tandem junction devices with an amorphous n-layer at the recombination junction (A) and with microcrystalline n-layer at the recombination junction (B).
Task II: Non-Semiconductor Research

This task consists of front and rear contacts to the multijunction devices and modules. We have optimized textured tin oxide deposited by atmospheric chemical vapor deposition (APCVD), for transmission, haze and sheet resistance. This has resulted in a gain of approximately 5% in the short-circuit current of single junction devices. We have also developed a low-pressure chemical vapor deposition (LPCVD) process for the front contact. Table I shows a comparison of the photovoltaic parameters of single junction devices fabricated on tin oxide and on zinc oxide front contacts. Clearly, substantial gains in current are observed for ZnO, but the $V_{oc}$ and the fill-factor needs to be improved.

<table>
<thead>
<tr>
<th></th>
<th>APCVD Tin Oxide</th>
<th>LPCVD Zinc Oxide</th>
<th>LPCVD Zinc Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission (%)</td>
<td>79</td>
<td>83</td>
<td>81.5</td>
</tr>
<tr>
<td>Haze (%)</td>
<td>16</td>
<td>15</td>
<td>31</td>
</tr>
<tr>
<td>Resistance (Ohm/Sq)</td>
<td>22</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>Fill Factor</td>
<td>0.74</td>
<td>0.74</td>
<td>0.69</td>
</tr>
<tr>
<td>$V_{oc}$ (V)</td>
<td>0.94</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>$J_{sc}$ (mA/cm$^2$)</td>
<td>10.5</td>
<td>11.1</td>
<td>11.4</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>7.3</td>
<td>6.9</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Table I Comparison of a cell prepared on APCVD Tin Oxide and 2 cells on LPCVD Zinc Oxide.

<table>
<thead>
<tr>
<th>Module #</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA)</th>
<th>FF</th>
<th>Efficiency (%)</th>
<th># of segments/seg.aper.area (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M2270-1</td>
<td>33.88</td>
<td>344.8</td>
<td>0.639</td>
<td>9.3</td>
<td>22/34.8</td>
</tr>
<tr>
<td>A3291-1</td>
<td>37.75</td>
<td>350.8</td>
<td>0.683</td>
<td>10.15</td>
<td>25/34.8</td>
</tr>
<tr>
<td>A2293-1</td>
<td>33.56</td>
<td>355.3</td>
<td>0.687</td>
<td>10.30</td>
<td>22/34.8</td>
</tr>
<tr>
<td>A309-1</td>
<td>36.18</td>
<td>359.4</td>
<td>0.669</td>
<td>10.47</td>
<td>24/34.8</td>
</tr>
</tbody>
</table>

Table II Photovoltaic parameters (initial) of some triple junction modules.

<table>
<thead>
<tr>
<th>Module #</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA)</th>
<th>FF</th>
<th>Efficiency (%)</th>
<th># of segments/seg.aper.area (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D309-2</td>
<td>63.23</td>
<td>209.5</td>
<td>0.675</td>
<td>11.35</td>
<td>25/30.35</td>
</tr>
<tr>
<td>D2076-2</td>
<td>58.56</td>
<td>204.7</td>
<td>0.682</td>
<td>11.24</td>
<td>24/20.35</td>
</tr>
<tr>
<td>M3097-1</td>
<td>62.57</td>
<td>225.3</td>
<td>0.669</td>
<td>11.05</td>
<td>25/23.18</td>
</tr>
<tr>
<td>M3093-1</td>
<td>62.39</td>
<td>221.4</td>
<td>0.684</td>
<td>10.95</td>
<td>26/23.18</td>
</tr>
<tr>
<td>M3091-1</td>
<td>62.75</td>
<td>203.0</td>
<td>0.685</td>
<td>11.05</td>
<td>26/20.35</td>
</tr>
</tbody>
</table>

Table III Photovoltaic parameters (initial) of some tandem junction modules.
Task III: Module Research

We have incorporated the improvements made in intrinsic amorphous silicon and microcrystalline doped layers in multijunction devices and large area modules. Figure 4 shows the initial J-V characteristics of a 11.1% efficient a-Si/a-SiGe tandem junction cell measured at NREL. Figure 5 shows the light-soaking behavior of a 10.5% efficient tandem module which had a conversion efficiency of 8.9% after 1000 hours of light-soaking. The initial photovoltaic parameters of several triple junction and tandem junction modules are tabulated in Tables II and III respectively. Figure 6 shows the light-soaking behavior of several triple junction modules. The best stabilized performance of a triple junction module was ~9% after 600 hours of light soaking.

Figure 4 J-V characteristics of an a-Si/a-SiGe tandem junction solar cell.

Figure 5 Efficiency as a function of light-soaking time for a 10.5% efficient tandem junction module.

Figure 6 Light induced degradation as a function of time for several triple junction modules.
**Title:** Research on Stable, High-Efficiency Amorphous Silicon Multijunction Modules

**Organization:** United Solar Systems Corp.
Troy, Michigan


**Objective**

The principal objective of the program is to conduct research on semiconductor materials and non-semiconductor materials to enhance the performance of multi-bandgap, multijunction, large-area amorphous silicon-based alloy modules. The goal is to demonstrate stabilized module efficiency of 10% for multijunction panel of area greater than 900 cm².

**Approach**

Double-junction and triple-junction cells are made on Ag/ZnO back reflector deposited on stainless steel substrates. a-SiGe alloy is used for the i-layer in the bottom and the middle cells; the top cell uses a-Si alloy. After evaporation of antireflection coating, silver grids and bus bars are put on the top surface, and the panel is encapsulated in an EVA/Tefzel structure to make a one-square-foot monolithic module.

**Status/Accomplishments**

**Component Cell Stability**

In order to obtain improved performance of both double- and triple-junction modules, we have made component cells for the two cases and have studied their performance both in initial and light-soaked conditions. In our study, a-Si alloy was used for the top cells, and the bottom cells used amorphous silicon germanium (a-SiGe) alloy. For middle cells, both a-Si and a-SiGe alloys were used. The thicknesses of the cells were chosen so as to provide short-circuit current density as appropriate for the multijunction structure. The top and middle cells were deposited on textured substrate without any back reflector, since in the multijunction configuration these cells do not see much reflected light. The bottom cells were deposited on our conventional silver/zinc oxide (Ag/ZnO) textured back reflector.

Typical initial performances for state-of-the-art component cells for the triple-junction structure are shown in Table I [1]. Also shown are the values after filtered one-sun (metal-arc lamp), 50 °C, 600 h light soaking. In this experiment, component cells were degraded under open-circuit condition at 50 °C for 600 h and measured at 25 °C. The top cell was degraded under one sun and measured under AM1.5 illumination; the middle cell was degraded under one sun with a
530 nm cut-on filter and measured under AM1.5 illumination with the same filter; the bottom cell was degraded under one sun with a 630 nm cut-on filter and measured under AM1.5 illumination with the same filter. We notice a degradation of 10% to 20% after light soaking. We should mention that one can improve the initial performance by making the component cells thicker, but this results in larger degradation and lower light-degraded efficiency.

We note that the component cells degrade between 9 to 18%. Similar studies [1] done on component cells for double-junction structure show a top cell degradation of 12% and a bottom cell degradation of 18%. If one designs the multijunction structure in a way so as to make the operation limited by the top cell current, one would expect to see a lower degradation in triple-junction cells than that in double-junction ones.

We should point out that the top cell in our structure does not use any carbon. By using hydrogen dilution to improve the quality of the i-layer, we have obtained for the top cell an initial open-circuit voltage ($V_{oc}$) of 1.023 V, a fill factor (FF) of 0.77 and a short-circuit current density ($J_{sc}$) of 7.4 mA/cm$^2$. This is the best performance of the top cell as reported in the literature.

**Module Results**

A large number (about 200) of double-junction modules has been made over the last two years incorporating optimizations involving component cells, "tunnel" junctions, uniformity and module loss. This resulted in a significant progress in the improvement of module efficiency as indicated in Fig. 1 [2,3]. The program on fabrication of one-square foot modules on Ag/ZnO back reflector started in September 1991, and in a period of less than two years, the initial module efficiency has increased from 7.5% to 11.4%. The best results achieved to date are shown in Table II where the initial efficiencies for one-square-foot modules as measured in our laboratory under a Spire 240A simulator are shown. Also shown are the measurements at NREL on the same modules both under a Spire simulator and also outdoors. Note the excellent agreement in all the three measurements.

The efficiency of 11.4% as measured at NREL on our module is the highest confirmed by them for any thin film photovoltaic module. The module characteristics are as follows: $V_{oc}$ = 1.68 V, $J_{sc}$ = 10.18 mA/cm$^2$ and FF = 0.67.

Although most of our efforts to date have been on double-junction modules, we have recently started optimization of triple-junction modules as well. Both the bottom and the middle cells use a-SiGe alloy and the top cell uses a-Si alloy. The highest efficiency obtained is 10.8% with $V_{oc}$ = 2.47 V, $J_{sc}$ = 6.37 mA/cm$^2$ and FF = 0.683. Further optimization of the modules is in progress.

We have also investigated the light-induced degradation of both double- and triple-junction modules. The results are shown in Fig. 2. The double-junction module had an initial efficiency of 11.1%, and the triple-junction module had an efficiency of 10.8%. Both stabilized around 9.5% indicating that triple-junction modules have better stability. It is also apparent from Fig. 25 that both the modules show true saturation in degradation after prolonged light exposure. This has important commercial implication since the modules can be rated at their stabilized efficiency values.
References


Table I. Present status at USSC of typical initial and degraded cell parameters for component cells degraded and measured under conditions described in the text. The high- and the mid-bandgap cells use Cr as back reflector. Use of Ag/ZnO as back reflectors for these cells increases $J_{sc}$ by 30% to 40%.

<table>
<thead>
<tr>
<th>Component Cell Type</th>
<th>Parameter</th>
<th>Initial</th>
<th>Degraded</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si high-bandgap cell</td>
<td>$J_{sc}$ (mA/cm²)</td>
<td>7.3</td>
<td>7.2</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>$V_{oc}$ (V)</td>
<td>1.01</td>
<td>0.98</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>FF</td>
<td>0.75</td>
<td>0.71</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>$P_{max}$ (mW/cm²)</td>
<td>5.53</td>
<td>5.01</td>
<td>0.52</td>
</tr>
<tr>
<td>a-Si mid-bandgap cell</td>
<td>$J_{sc}$ (mA/cm²)</td>
<td>6.44</td>
<td>6.2</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>$V_{oc}$ (V)</td>
<td>0.90</td>
<td>0.87</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>FF</td>
<td>0.70</td>
<td>0.61</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>$P_{max}$ (mW/cm²)</td>
<td>4.02</td>
<td>3.29</td>
<td>0.73</td>
</tr>
<tr>
<td>a-SiGe mid-bandgap cell</td>
<td>$J_{sc}$ (mA/cm²)</td>
<td>7.02</td>
<td>6.85</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>$V_{oc}$ (V)</td>
<td>0.77</td>
<td>0.74</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>FF</td>
<td>0.65</td>
<td>0.57</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>$P_{max}$ (mW/cm²)</td>
<td>3.51</td>
<td>2.89</td>
<td>0.62</td>
</tr>
<tr>
<td>a-SiGe low-bandgap cell</td>
<td>$J_{sc}$ (mA/cm²)</td>
<td>7.8</td>
<td>7.7</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>$V_{oc}$ (V)</td>
<td>0.67</td>
<td>0.65</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>FF</td>
<td>0.64</td>
<td>0.56</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>$P_{max}$ (mW/cm²)</td>
<td>3.34</td>
<td>2.80</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table II. Summary of Module Results.

<table>
<thead>
<tr>
<th>Module No.</th>
<th>Measurement Site</th>
<th>Measurement Type</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2178</td>
<td>NREL</td>
<td>Indoor</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>NREL</td>
<td>Outdoor</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>USSC</td>
<td>Indoor</td>
<td>11.3</td>
</tr>
<tr>
<td>2180</td>
<td>NREL</td>
<td>Indoor</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td>NREL</td>
<td>Outdoor</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>USSC</td>
<td>Indoor</td>
<td>11.2</td>
</tr>
<tr>
<td>2185</td>
<td>NREL</td>
<td>Indoor</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>NREL</td>
<td>Outdoor</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>USSC</td>
<td>Indoor</td>
<td>11.2</td>
</tr>
</tbody>
</table>
Fig. 1. Progress in initial module efficiency at USSC.

Fig. 2. Light-induced degradation in module efficiency.
Title: Small Angle X-ray Scattering of Amorphous Silicon-Based Semiconductors

Organization: Department of Physics, Colorado School of Mines, Golden, Colorado

Contributors: D.L. Williamson, principal investigator; S.J. Jones and Y. Chen

Objectives

During the last few years we have been applying a direct structural technique based on the diffraction of x-rays to determine quantitatively some aspects of the microstructure of a-Si:H and the related alloys, a-SiGe:H and a-SiC:H. This somewhat uncommon technique, small-angle x-ray scattering (SAXS), is proving to be a powerful and valuable probe. Our general objectives are to provide new details of the microstructure for the size scale from about 1 to 30 nm in high-quality a-Si:H and related alloys prepared by current state-of-the-art deposition methods as well as by new and emerging deposition technologies and thereby to help determine the role of microvoids and other density fluctuations in controlling the opto-electronic properties.

More specifically, the objectives are to determine whether the presence of microstructure as detected by SAXS (i) limits the photovoltaic properties of device-quality a-Si:H, (ii) plays a role in determining the photo-stability of a-Si:H, and (iii) is responsible for degradation of the photovoltaic properties due to alloying with Ge, C and other constituents.

Approach

The approach involves collaboration with several groups that can supply relevant systematic sets of samples and the associated opto-electronic data to help address the objectives. Since the SAXS technique has not been a standard characterization technique for thin-film materials, the project involves considerable development of the method with regard to standardizing the procedures, minimizing substrate influences and implementing improved data reduction and modeling methodology. Precise, highly reproducible, and accurate results are being sought in order to allow useful, reliable, and sensitive comparisons of materials deposited under different conditions, by different methods, and by different systems that represent the same nominal method. The SAXS measurements are supplemented by in-house flotation density, Raman spectroscopy, x-ray diffraction, and annealing studies of the same films used for the SAXS.

We have made SAXS and flotation density measurements of numerous a-Si:H thin films prepared by rf glow-discharge (PECVD), hotwire filament (HW), reactive dc magnetron sputtering (RMS), and electron cyclotron resonance (ECR). Several of these samples can be characterized as "device quality" on the basis of their photoresponse and other opto-electronic properties. Deposition variables of particular interest were the effects of plasma power (primarily to change deposition rate), of various diluting gases (H₂, Ar, He, and Xe), and of higher substrate temperatures. Suppliers of a-Si:H films produced by the various deposition methods included: PECVD - USSC, Ecole Polytechnique (Paris); high-frequency PECVD - Univ. Neuchatel; HW-NREL; RMS - Univ. Illinois; and ECR - JPL.

Several sets of a-SiGe:H alloys from various groups have been analyzed. These include PECVD films from NREL, Solarex, USSC, Stuttgart University, IACS.
Several samples of a-SiC:H films prepared by reactive dc magnetron sputtering, RMS, (U. Illinois) and by PECVD (Solarex) have been analyzed. Methane was the source of the C in both cases.

Results

The SAXS technique is able to provide microstructural information not available from other methods and with a high degree of sensitivity. It is particularly sensitive to microvoids and the presence of oriented microstructure. The latter is readily associated with columnar-type growth and can even be observed in premature stages not detectable by TEM.

In general, the SAXS-detected microstructures of a-Si:H, a-SiGe:H, and a-SiC:H are quite distinct. The residual microstructure in the best quality a-Si:H (as indicated by solar cell efficiencies, photoconductivities, and defect densities) corresponds to voids or low density regions comprising well below 1 vol.% of the film.

The a-SiGe:H films yield quite similar, weak SAXS intensities up to about 20 at.% Ge above which a clear change in microstructure occurs corresponding to the growth of voids or low-density, H-rich regions that are 3 to 4 nm in size. This change is also associated with the formation of an oriented microstructure that may be a precursor to columnar-type growth. This result suggests that changes in deposition conditions that would enhance the surface mobility of the depositing species need to be developed for the higher germane-to-silane ratios in the plasma. We have obtained considerable data showing that the H-dilution method of enhancing surface mobilities does indeed usually lead to reduced SAXS-detected microstructure.

Addition of relatively small amounts of C lead to sharp increases in SAXS of a-SiC:H alloys prepared by PECVD. The high density of extremely small scattering centers may be associated with the incorporation of CH\_3 in the films, consistent with our earlier work on one set of PECVD alloys from NREL. Much less evidence for oriented microstructure is observed for the a-SiC:H alloys compared to a-SiGe:H alloys.

Specific conclusions from the research during FY93 are as follows: (see the publications indicated for details)

(a) Dilution during 70 MHz PECVD growth with Ar causes enhanced microstructure in the form of microvoids. High Ar dilution leads to a highly oriented microstructure consistent with columnar-like growth. This behavior correlates with opto-electronic degradation\(^1\). He dilution during PECVD growth appears to allow increased deposition rates while maintaining low microvoid content and little or no oriented microstructure\(^1\).

(b) Both the ECR and RMS a-Si:H films show that high photo/dark conductivity ratios and significantly more microstructure can coexist\(^2\), however solar cells have not yet been fabricated with these alternate deposition methods.

(c) a-SiGe:H alloys that show a microstructural transition corresponding to enhanced columnar-like growth above Ge contents of about 20 at.% have corresponding sharp degradations in opto-electronic properties above this same Ge content\(^3\). This provides strong evidence that the increased low-density heterogeneity is directly responsible for the degradation.

(d) Solar cells made from a-SiGe:H alloys have efficiencies that decrease smoothly with increasing Ge addition while SAXS from the corresponding alloys shows little change in the microstructure until Ge contents reach 30 and 41 at.%\(^4\) (similar to the Stuttgart sample results versus Ge content). Thus, an obvious correlation of SAXS and the initial cell efficiencies was not found. However, the cell stability for the latter two Ge contents was noticeably poorer\(^4\).

(e) a-SiGe:H:F alloys prepared from silane and germanium fluoride at Princeton
are microstructurally different from all the other PECVD alloys in that a larger fraction of smaller scattering centers are present in a more randomly oriented array\(^2,5\).

(f) a-SiC:H alloys prepared by RMS all have a higher degree of oriented microstructure in contrast with PECVD materials which have randomly oriented or spherical microvoids\(^5\). The RMS material has lower amounts of SAXS-detected microstructure and higher film densities for similar C contents. The average void size is smaller in the PECVD films\(^5\).

(g) Interdiffusion is negligible between the aluminum foil substrate (used to prepare the films for SAXS) and the a-Si:H provided substrate temperatures are below 450 °C\(^6\).

(h) Modeling of the sample tilting effects on the SAXS intensities due to oriented scattering centers is possible on the basis of a distribution of ellipsoidal voids\(^2\).

References

Objectives

Transparent conducting materials are essential components of many kinds of solar cells, in which they serve as front-surface electrodes. In tandem cells, back surface electrodes also need to be transparent. Finally, some designs for highly reflective back contacts also call for a transparent conducting layer. The compositions of these transparent conducting layers are usually based on oxides of tin, indium and/or zinc, and are hence referred to as transparent conducting oxides (TCO). In addition to having low electrical resistance and low optical absorption, the structure of a TCO must minimize reflection losses. The TCO must also resist degradation during cell fabrication and use. Finally, the method for making the TCO must be inexpensive and safe.

Our general objectives are to improve the performance of TCO materials and the methods for their production. We aim to reduce their electrical resistance, optical absorption and reflection losses, and to lower the deposition temperature to avoid thermal degradation of other cell components. For the production method, the prime consideration is to deposit the TCO layers at a high rate with relatively simple apparatus. The method chosen is chemical vapor deposition at atmospheric pressure (APCVD), since it has been demonstrated in the glass-coating industry to be the most cost-effective method for making large areas of TCO coatings.

Background on Textured Fluorine-Doped Zinc Oxide Films

Zinc oxide is a promising material for forming less expensive TCO layers, since zinc metal is much less expensive than tin or indium. Also, zinc is much more abundant in the earth's crust, than is tin or indium, so that even large-scale use of solar cells would not lead to any shortage of zinc. Also, zinc is widely distributed on earth, and is mined in many countries, so continuity of supply is assured in any kind of political situation. In contrast, tin is mined in large quantities in only a few countries.

We discovered that fluorine can be used to dope zinc oxide to very high electron mobility, and therefore very high transparency. The absorption loss in fluorine-doped zinc oxide is less than half of the loss in fluorine-doped tin oxide having the same sheet resistance[1,2], or in zinc oxide doped with boron[3], aluminum[4] or gallium[5] instead of fluorine. Fluorine is also a preferred dopant for zinc oxide, because it is known to be electrically inactive, or even beneficial, in hydrogenated amorphous silicon.

The fluorine-doped zinc oxide is produced by CVD from diethyl zinc, ethanol and hexafluoropropene at atmospheric pressure, in the temperature range 375 to 450 C. Films deposited under these conditions show good adhesion to the glass substrates (Scotch tape test). The highest electrical conductivity and light transmission are found for films deposited at the highest temperatures (450 C), and containing about 0.5 atomic percent fluorine. With this material, we could produce a TCO with a sheet resistance of 5 ohms per square and a visible absorption loss of only about 3%, at growth rates up to 250 nm/minute.
We discovered that the amount of texture (roughness) of the zinc oxide films depends dramatically on the amount of water vapor in the growth atmosphere. Small amounts of water vapor (about 1\% of the ethanol concentration) produce smooth films, but decreasing the water content to less than 0.25\% of the ethanol content produced textured (rough) zinc oxide films suitable for efficient light-trapping in solar cells. Eliminating the water entirely, however, almost completely eliminated film growth, so a small, controlled source of water vapor is essential to control of film texture[1].

Substrate Effects on the Growth of Zinc Oxide

In order to deposit the best quality fluorine-doped tin oxide on low-cost soda-lime glass, it is necessary to place a sodium barrier, such as silica, on the glass before depositing the tin oxide. We have discovered that there is no such sodium degradation of fluorine-doped zinc oxide. The conductivity and transparency of ZnO:F is just as high when it is deposited on high-sodium glass as on sodium-free substrates. Thus no sodium barrier needs to be deposited on soda-lime glass prior to coating it with ZnO:F. This should lower the cost of producing a high-quality TCO by eliminating one processing step, production of the sodium barrier normally needed under fluorine-doped tin oxide. The lower deposition temperatures for zinc oxide (450 C instead of 550 C or more for SnO2:F) also result in much less warpage to the glass plates.

Zinc oxide is also used as a transparent conductive diffusion barrier which also enhances the reflectivity of back-surface reflectors on amorphous silicon solar cells. Such zinc oxide layers are normally made by reactive sputtering. We succeeded in growing textured fluorine-doped zinc oxide on silver-coated steel substrates by first nucleating the surface using the fast reaction of diethylzinc and water vapor and then continuing the growth with ethanol to produce a textured conductive layer. Solar cells were grown on these layers at Energy conversion Devices. The cells were comparable to those typically grown on their standard sputtered zinc oxide, despite the higher transparency and conductivity of the CVD ZnO:F.

Solar Cell Deposition on Zinc Oxide Films

Samples of fluorine-doped zinc oxide films were sent to Solarex Corporation, where amorphous silicon solar cells were grown on them. Their measurements of short-circuit currents confirmed that the optical absorption in fluorine-doped zinc oxide is remarkably smaller than in other TCO materials. Their cells grown on zinc oxide, however, also had lower open circuit voltages and fill factors than ones grown on conventional tin oxide.

Cells were also made on our ZnO:F at the Institute for Energy Conversion at the University of Delaware. Only an insignificant reduction (about 10 mV) of the open circuit voltage was found on these cells, compared to standard cells made on fluorine-doped tin oxide in the same run. Detailed evaluation of these cells showed that a higher contact resistance seems to develop at the interface between the zinc oxide and the amorphous silicon. Studies are underway to determine the origin of this contact resistance, and to find ways to eliminate it.

One approach to reducing this contact resistance is to cover the ZnO:F with a thin layer of fluorine-doped tin oxide, which is the standard material on which amorphous silicon cells are grown. We made initial samples of such bilayer coatings with the use of CVD from tetramethyltin, oxygen and hexafluoropropene at a temperature of 480 C. This temperature is a compromise. Higher substrate temperatures would produce SnO2:F of higher conductivity at higher growth rates, but we found that temperatures above 480 C reduced the conductivity of previously-deposited ZnO:F films. Initial samples of these bilayers were furnished to cooperating team members at the Institute for Energy Conversion and at Iowa State University.
Development of Zinc Oxide Layers which are Compatible with New Amorphous Silicon Processing Requirements

In order to provide zinc oxide films with more uniform thickness as substrates for growth of solar cells, a new deposition apparatus was constructed. It consists of a long furnace with a moving platform, constructed by BTU Engineering, and a CVD nozzle built by the Watkins-Johnson Company. The gas-handling system was designed and built at Harvard. This equipment has made films with thickness uniformity of ±10% over an area of 10 cm by 10 cm.

Tests with this equipment showed that in order to produce highly conductive and transparent films, the reactant gases must be introduced in such a way that the diethylzinc vapor mixes with the alcohol vapor just before they reach the surface of the substrate. If, instead, the pure diethylzinc vapor reaches the surface first, then it decomposes to produce a film that has low conductivity and low transparency.

Growth and Bonding Theory

Our density functional theory of chemical bonding has been developed further, and programs written to carry it out. The theoretical energy and structure were found to be in good agreement with experiments on alpha-quartz and on alpha-cristobalite [6]. The new bonding theory has also been applied to two other phases of silicon dioxide which are stable at high pressures. The structure and energy of these phases are in good agreement with the calculations, and the pressures of the phase transitions are also in general agreement with experiment [7]. The calculations will be extended to zinc oxide and tin oxide in the future; however, at present, higher immediate priorities were identified to meet the goals of the amorphous silicon team effort.

Conclusions

- Textured fluorine-doped tin oxide films with high electrical conductivity (5 ohms/square) and low optical absorption (3%) were produced by chemical vapor deposition at atmospheric pressure (APCVD) on soda-lime glass substrates at about 450 C, at moderate deposition rates (up to 250 nm per minute). No diffusion barrier layer was needed between the high-sodium glass and the fluorine-doped zinc oxide.

- Amorphous silicon solar cells grown on these textured films show very high quantum efficiencies, which demonstrates the high light-trapping ability of this texture, and the high transparency of the zinc oxide film. However, a significant contact resistance develops at the interface between the amorphous silicon and the zinc oxide.

- Transparent, highly conductive fluorine-doped tin oxide films were grown by APCVD at temperatures around 480 C on top of textured transparent conductive fluorine-doped zinc oxide. These bi-layers should be suitable for low-resistance contact to p-type amorphous silicon on the front surface of a solar cell.

References

Objective

The major objective of the program is to develop alternative deposition techniques and new device designs for improving the performance and stability of a-Si:H and a-(Si,Ge):H solar cells.

Material Growth

Two techniques were used to deposit the materials.

1. Low pressure remote Electron-Cyclotron-Resonance (ECR) deposition. In this technique, remote H or He plasma beams generated using an ECR discharge were used to decompose silane and deposit a-Si:H. We found a pronounced difference between the properties of a-Si:H films deposited using Hydrogen vs. He. In particular, the growth rates were significantly lower when H was present in the plasma beam, indicating significant etching of the film during growth. With H plasma, we could deposit high quality a-Si:H films at higher temperatures (350-375°C). These films, in general, tended to be more stable than comparable films deposited using He as the plasma gas. These films also had a higher bandgap (1.72-1.8 eV) compared to He-plasma films, whose bandgaps could be reduced to the 1.65 eV range under appropriate deposition conditions.

2. The second technique we used for depositing films was high H dilution in a RF triode reactor. This technique was successfully used to deposit high quality a-(Si,Ge):H films. Typical H dilution was 15:1 in the gas mixture. The films were subjected to a negative bias during growth. Using this combination of negative bias and high H dilution, we were able to grow a-(Si,Ge):H films and devices quite reproducibly.[1]

Improved Stability of a-Si:H films

We discovered that the stability of a-Si:H films grown using H plasma beam in the ECR reactor could be improved quite significantly by using sub ppm compensation with B. Sub ppm levels of B reduce the dark conductivity, and also reduce the Staebler-Wronski effect. In Fig. 1, we show the influence of B compensation on the increase in sub-gap defect density upon light soaking. It is
clear from the figure that there is an appropriate amount of B which leads to both the lowest initial and lowest degraded defect densities. We relate this phenomenon to the influence of B on the residual donor-type impurities in the material. B may form a donor-acceptor pair with the residual donors (e.g. O or N), and thereby reduce the deleterious effect of donors on the electronic properties of the material.[2,3,4]

**Improved stability of devices by using bandgap grading**

We have shown earlier that the stability of the devices can be expected to improve when the bandgap of the i layer is graded, since grading can introduce an additional electric field in the middle regions of the i layer, thereby assisting in hole transport.[5] During this year, we actually fabricated a-Si:H devices using the RF triode reactor where we graded the bandgap as shown in Fig. 2. The typical I(V) curve of the device is shown in Fig. 3, and its stability, compared to a standard ungraded cell, is shown in Fig. 4. It appears that the grading strategy indeed improves the stability of the device.[5] Further work is in progress to improve the grading, by using the more extensive set of bandgaps available in the ECR reactor.

**Materials and Devices in a-(Si,Ge):H**

We have fabricated devices in a-(Si,Ge):H. These were standard p-i-n type devices, deposited on SnO2 substrates. The devices had a specially graded buffer layer, and graded bandgap i layer, where the grading followed a strategy similar to the one shown in Fig. 2. The typical I(V) curve for a device is shown in Fig. 5, and its quantum efficiency in Fig. 6. It appears from both the I(V) curve and the QE data that the material being deposited using high H dilution is device quality.[1]

**References:**


Fig. 1

Influence of ppm B doping on subgap absorption and stability

Fig. 2

Band diagram of graded gap a-Si:H solar cell

Fig. 3

I(V) curve of graded gap a-Si:H solar cell

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Fig. 4
Stability of graded gap cell compared to stability of ungraded a-Si:H solar cell.

Fig. 5
I(V) curve of a-(Si,Ge):H solar cell.

Fig. 6
Quantum efficiency of a-(Si,Ge):H solar cell.
Several different types of measurements have indicated that hydrogenated amorphous silicon (a-Si:H) and alloy films are highly inhomogeneous, with many small regions of depleted Si and of clustered H. These film inhomogeneities are implicated in the quality and stability limitations of a-Si:H photovoltaics and films.

The program is directed to achieving an improved understanding and direct observation of these atomic-scale inhomogeneities, and how they depend on film-growth parameters. This is being done by studying the atomic scale topology of the film surface with a scanning tunneling microscope (STM). In the previous year we studied films deposited by rf discharge deposition in our deposition chamber, and transferred without air exposure into our STM. This year we developed and tested a method for transferring films made at other laboratories to our STM, with a total of a few minutes of air exposure. We have successfully tunneled on these films, and have now used this technique to study several types of films produced at NREL. These observations will be summarized below. All of the data were taken using high resolution and aspect-ratio STM probes, which taper at 45-70° to a <0.5 nm radius point, providing an ability to observe high angle surface structures and voids.

Technical Approach

Intrinsic a-Si:H by rf discharge

We have studied the surface topology of ~300 nm thick, intrinsic films, deposited by rf discharge at NREL in a system that produces high efficiency a-Si:H photovoltaics. We had previously studied films made under nominally equivalent deposition conditions in our laboratory, but none of these have been incorporated into devices. Thus, this provides an essential test of the applicability of our in-house results to device-quality films. The typical surface topology observed is shown in Fig. 1. This type of topology, with ~5 nm of height variations mostly in the form of ~200 nm width hills, was observed on many regions of the film surface. None of the valleys between these hills are steep enough to suggest a growing void region, due to shadowing by surrounding steep hill sides. Although many similar regions were observed on the films grown in our laboratory, the latter also contained occasional atomically smooth regions as well as some steep-sided, void growth regions. These differences are thought to be a result of different film-growth mechanisms, not the brief air exposure of the NREL film. Deposition chamber and electrode-geometries, gas flow patterns, fringing fields, temperature gradients and many other factors differ between the in-house and the NREL deposition chambers.
Fig. 1 A STM image of a 300 nm thick intrinsic a-Si:H film grown at $T_s = 210^\circ C$ by the rf glow discharge technique on a crystal Si substrate. The vertical scale has been expanded $3\times$ for clarity.

Fig. 2 A higher resolution image of the same film as Fig. 1. The vertical scale is not expanded.
Fig. 3  A STM image of a 500 nm thick n-doped a-Si:H film grown at $T_s = 210^\circ$C by the rf glow discharge technique on a crystal Si substrate. The vertical scale is expanded 3×.

Fig. 4  A STM image of a 200 nm thick a-Si:H film grown by the hot wire method on a crystal Si substrate. The tunneling bias was 4.0 V with a tunneling current of 0.040 nA. The vertical scale is expanded 3×.
n-type a-Si:H by rf discharge

The same NREL deposition chamber was used to deposit $\sim 10^2 \, \Omega \text{cm}$, phosphorous-doped, 500 nm thick film, from silane plus phosphene. The region shown in Fig. 2 is typical of this film surface. It is also very similar to the surface topology of the film in Fig. 1, indicating that heavy phosphorous doping has not introduced significant new film-growth inhomogeneities. Again, all regions studied have this overall appearance.

Intrinsic a-Si:H by hot-wire deposition

Films grown by silane decomposition on a hot tungsten wire stretched directly above the substrate have been shown to yield unique, low H-content a-Si:H films with excellent electrical properties.\(^2\) To see if this deposition method may result in structural differences in the films, we have studied the surface topology of films grown by this method. We have initially studied the surfaces of films grown at NREL with a more typical, $\sim 10\%$, H content; an example is given in Fig. 3. There one sees that the general character of the surface topology is very similar to that in Fig. 1 and 2. Whereas small angle x-ray scattering (SAXS) observations on such "hot-wire" films indicate an increased fraction of large voids,\(^3\) we observe no indication of true voids in the material. Since a STM detects the conducting surface of the film, this suggests that the SAXS observations may be detecting low Si-density regions rather than complete voids of silicon atoms and of conduction.

Conclusions

Perhaps the most striking aspect of the film-growth surfaces seen in the above figures is their overall roughness. This is enhanced in the figures by an expansion of the height scale to show more detail, but it nonetheless indicates a highly inhomogeneous film growth. This inhomogeneity is not considered in any current growth models, yet may be a key characteristic in a-Si:H photovoltaics. We have previously suggested a variety of possible causes.\(^1\) The next most striking observation is the similarity of these surface topologies on different films. While very small ($< 2 \, \text{nm}$) inhomogeneities are not observable in the scale of these figures, higher resolution pieces of smaller areas of these films also indicate an absence of complete voids (e.g. Fig. 2). It appears that complete conductivity voids of $> 0.5 \, \text{nm}$ size do not occur very frequently; low Si-density regions rather than zero density regions are implied. Another interesting observation is an absence, in these film surfaces, of several quite different types of surface topologies seen on films prepared in our deposition chamber under nominally identical conditions. In addition to many areas like those shown above, our films had occasional flat surface regions, as well as some clustered void regions.

References

1. Research Objectives

a. To prepare thin films of µc-Si and a-Si,N:H alloys; to characterize their microstructure and chemical bonding; and to study selected optical and electrical properties that have been deemed important in the determining the applicability of these materials as photo-active i-region candidates in tandem photovoltaic devices.

b. To understand and explain any special or unique electrical and/or optical properties of µc-Si and a-Si,N:H alloys in terms of microscopic models that focus on the microstructure and/or local chemical bonding arrangements.

2. Research Approach

a. Film deposition: Thin films of µc-Si doped with boron have been prepared by remote PECVD, and by reactive magnetron sputtering. Thin films of a-Si,N:H have been prepared by remote PECVD from the Si-atom source gas SiH4, and using two different N-atom source gases, N2 and NH3.

b. Chemical and structural characterization: Chemical characterization has been performed by IR spectroscopy, and SIMS. Structural characterization has been done by high resolution TEM, and Raman scattering spectroscopy.

c. Electrical and optical studies: These measurements include: (i) optical absorption, (ii) CPM, (iii) steady-state photoconductivity, (iv) dark conductivity, (v) light-soaking, and (vi) minority carrier transport by the SSPG method.

d. Device studies: Majority carrier transport in a-Si:H, and µc-Si have been determined from measurements of the transconductance in TFT devices.

e. Model and theory chemical bonding studies: These have focused on explaining (i) the dark conductivity transport in doped µc-Si, (ii) the mechanism for N-atom doping in a-Si:H, and (iii) a possible microscopic explanation for the Staebler-Wronski effect in a-Si:H.

3. Significant Research Results

(a) Light-Inducted Transport Property Changes in µc-Si

We have studied light-induced changes in the transport properties of B-compensated µc-Si by two techniques. The samples used in these studies were prepared by remote PECVD, and the most-closely compensated samples were selected by monitoring the dark conductivity and dark conductivity activation energy as a function of the B2H6/SiH4 source gas mixture. The B-atom concentrations, as determined by SIMS, in these samples were in the range of 4-8x10^17 cm^-3. Similar results were also obtained for B-compensated µc-Si samples produced by reactive magnetron sputtering, RMS. The studies described below, as well as the TFT studies in e(ii) used the remote-PECVD-thin films. The majority carrier transport was studied by the decay of the photoconductivity under high-light levels of illumination (~200 mW/cm^2), and the ambipolar...
diffusion length, $L_{amb}$, was studied by the SSPG method at the same illumination levels. As noted in previous reports, for light soaking times of about 3 hours, there was no detectable drop in the photocurrent in µc-Si(B), as compared to a factor of ∼3 decrease in the photocurrent for a control device-grade a-Si:H sample. In contrast there was a small decrease in $L_{amb}$ for µc-Si, but this was about a factor of 3 less than for a-Si:H.

(b) Electrical and Optical Properties of a-Si,N:H Alloys

We have deposited films of a-Si,N:H by remote PECVD from N2 and SiH4 for N-concentrations, [N], to about 12 at.%. Bonded-H concentrations were ∼7 - 12 at.%. The H-atoms were mostly in Si-H groups, and with no IR detectable Si-NH. The films with [N] = 9-12 at.% have E04 bandgaps of ∼2.0 to 2.2 eV, which make them potentially useful as wide bandgap photo-active materials in tandem PV cells. These alloys do not display any evidence for an inhomogeneous microstructure when examined by HRTEM at lattice imaging magnifications. Several properties are of special interest for PV applications. First, like other a-Si:H-based alloys, the photoconductivity relative to a-Si:H is degraded by alloying. For alloys with E04, = 2 to 2.2 eV, this degradation is ∼50. Second, the ambipolar diffusion lengths, $L_{amb}$, obtained by the SSPG method, for films with [N] = 10 at.% and E04 ∼2.1 eV, are comparable to those of a-Si:H. For more lightly-nitrided films, $L_{amb}$ first decreases with respect to a-Si:H and then increases as [N] increases to 10 - 12 at.%. These trends follow the behavior of the dark conductivity activation energy, $E_a$, which initially drops due to doping (see section (e)), and then increases into the alloy regime for [N] > 5 at.%. For films with [N] ∼10 at.% the dark conductivities and $E_a$'s are comparable to those of undoped a-Si:H. Third, the magnitude of the Staebler-Wronski effect, as monitored by the photo- to dark-conductivity ratio after an ∼1 hour light soak, was about the same as in a-Si:H. Finally, we have contrasted the properties of these films with a-Si,N:H alloys with the same [N] and E04, prepared from an NH3 N-atom source gas, and attribute several differences in photoelectronic behavior; e.g., a significantly stronger Staebler-Wronski effect, to the presence of Si-NH bonding arrangements as detected by IR (see section (d)).

(c) Nitrogen as a dopant in a-Si:H Alloys

Many of the group III and V atoms which are substitutional dopants in c-Si, are also dopants in a-Si:H, suggesting that doping in a-Si:H is simply derived from the four-fold coordinated bonding arrangements of these atoms. However, analysis of NMR data for a-Si:H has shown that H-atoms are generally near-neighbors to these dopant atoms; e.g., as second nearest-neighbors to P, and nearest neighbors to B. The bonding arrangement for P is consistent with the a four-fold coordinated positively charged P-donor having about the same effective electronegativity as neutral O, and therefore also showing a preferential, and non-statistical association with second-neighbor H-atoms. This same type of bonding is expected to apply for other group V atoms in a-Si:H, even for N-atom which is not donor atom in c-Si. We have studied the incorporation of N-atoms in a-Si:H, focusing on the Si-rich regime from [N] = 0.5 to 10 at.% N in which such a transition from doping to alloy formation could occur. Using remote PECVD, and two N-atom source gases, N2 and NH3, we have observed a doping regime with dark conductivity activation energies of ∼0.4 eV for [N] < 2-3 at.%, followed by an alloy regime with higher activation energies for [N] > 5 at.%. This behavior is similar to what has been reported for a-Si,As:H. By analogy with a-Si,P:H, we attribute this doping to four-fold coordinated N-atoms with second neighbor H-atoms. The occurrence of this arrangement is supported by IR results, and by a chemical bonding model which demonstrates the equivalence in chemical potential of four-fold N+, and neutral O-atoms.

(d) A Microscopic Mechanism for the Staebler-Wronski Effect

We have studied the photo-electronic properties of a-Si,N:H alloys prepared by remote PECVD from two N-atom source gases - N2 and NH3. These studies have suggested that local bonding arrangements of H-atoms are involved in photo-degradation effects. Deposition conditions were
adjusted to give bonded-H concentrations of ~7-10 at.%. Studies focused on films with ~10 at.% N, and EQ4 bandgaps of 2.1-2.2 eV. Films from both sources with EQ4 ~ 2.1-2.2 eV have many properties that are essentially the same (i) dark conductivities, and dark conductivity activation energies, (ii) Si-H bond-stretching IR frequencies, (iii) photo-conductivities, and (iv) ambipolar diffusion lengths. However, their SW effects are markedly different with the photo-induced changes being three times greater in the films from the NH3 source gas. These films contain a relatively low concentration of Si-NH bonds (by IR), in addition to the Si-H bonds which dominate in films from both N-gases. Based on (i) this observation, (ii) the SW effect in a-Si:H films with different ratios of SiH to polyhydride, and (iii) quantum chemistry calculations, we propose that the bonding arrangements that are important in the SW effect are (a) Si-H groups, and (b) other H-atom groups like (-SiH2-)n and -Si-NH-Si-, which have lower local dimensionalities, and are encapsulated by Si-H terminated internal surfaces. The model is based on a H-exchange process that creates Si-dangling bonds (Si*) e.g., SiH + (-SiH2-) -> Si* + -HSi* + H3Si-, involving removal of H from an SiH site, and insertion into a polyhydride chain. A similar reversible reaction applies to films with Si-NH where insertion of H into -Si-NH-Si- can yield -Si* + H2Si- configurations. This model is supported by thermal annealing studies on near stoichiometric films of a-Si3N4:H, in which the bonded-H occurs in both SiH and SiNH groups.

(e) TFT Devices

(i) a-Si:H channels: We have optimized performance of a-Si:H TFTs by careful control of local bonding in the nitride layers of dual-layer Si-oxide-nitride dielectrics. It has been shown that Si-Si bonding groups in off-stoichiometric Si3N4:H thin films are precursors for Si-atom dangling bonds which act as traps for charged carriers. We have used on-line AES to monitor the local bonding of Si in low-temperature, 300°C, remote-plasma deposited silicon nitrides. We have tracked the changes in Si-bonding arrangements as a function of the source gas ratio, R, of NH3 to SiH4, and have determined a value of R that separates these a-Si,N :H films into two groups (a) alloys with Si-Si bonding, and (b) alloys with no AES-detectable Si-Si bonding. We have used IR to study the bonded-H groups, and have found that (a) Si-H bonding dominates in films with Si-Si bonding, (b) Si-NH bonding dominates in films with no detectable Si-Si bonding, but (c) the demarcation point between these two regimes for R of ~ 9-10, is not the R-value at which the total bonded-H concentration is minimized, so that films in which Si-Si bonding is not detected have both Si-H and Si-NH groups. We have found that the TFT transconductance, gm, which under some circumstances can be transformed into an effective mobility, is small in films with Si-Si bonding, R < 7, and then increases by a factor of 5-10 for films in which Si-Si bonding is not detected by AES, R =10. For these values of R, the effective mobilities are ~1.2 to 1.5 cm2/V-s. For the same values of R, the threshold voltage is minimized, and hysterisis in the C-V characteristics of MIS capacitors with single layer nitrides is also minimized. The on-off current ratio of the TFTs for a source-drain bias = 10 V and a gate voltage = 20 V is in excess of 107. We discuss improvements in TFT performance when n+ µc-Si source and drain contacts are substituted for the n+ a-Si:H contacts used in the TFTs described above.

(ii) µc-Si channels: A low-temperature, 300°C, remote plasma-enhanced CVD process has been used for the dielectric and semiconducting layers of bottom-gate TFTs. These layers are (a) 450Å of stoichiometric SiO2 with no IR-detectable bonded-H, (b) 2500Å of Si3N4:H, with no AES-detectable Si-Si bonding, and with bonded-H mostly in Si-NH arrangements, (c) 1000Å of boron-compensated intrinsic i-µc-Si with a dark conductivity activation energy of ~0.8 eV, and (d) 250Å of n+ µc-Si with a dark conductivity of ~ 5-10 S/cm. These in-situ depositions encapsulate the four interfaces of importance in device performance (a) the gate metal/SiO2 interface, (b) the internal dual-layer dielectric interface between SiO2 and Si3N4:H, (c) the Si3N4:H/i-µc-Si interface and (d) the i-µc-Si/n+ µc-Si interface. After the depositions (a) source and drain regions are defined by conventional photolithographic and etching techniques, (b) metal contacts are
applied, and (c) the back of the μc-Si channel is passivated to improve TFT performance. The most interesting property of these devices is their high transconductance, which correlates with an effective electron channel mobility of ~6.5 cm²/V·s. This value is significantly higher than that in a-Si TFTs fabricated at about the same temperature, but is lower by 5-10, than what has been reported for poly-Si TFTs processed at ~600°C. The transport limitation in the μc-Si is determined by its diphasic microstructure (see (f)). μc-Si consists of small, 1-200Å, Si crystallites encapsulated by a-Si:H layers of about the thicknesses. The transport limitation is set by the electron mobility in extended states of the a-Si:H component, ~10-20 cm²/V·s, so that performance of μc-Si TFTs can be expected to be improved by at most a factor of about two.

(f) Transport in μc-Si

The statistical shift of the Fermi level through the band-gap density of states, DOS, of a-Si:H provides a theoretical basis for the exponential M-N relationship between the dark conductivity prefactor, s~, and dark activation energy, E~*, namely s~* = C exp (E~*/E~O), with C = 2.5±1 S/cm and E~O = 0.12±0.02 eV. Data for i) undoped and doped a-Si,C:H, and μc-Si,C, and ii) undoped and lightly-doped μc-Si fall are fit with approximately the same positive values of E~O. Data for heavily-doped μc-Si displays an inverted M-N relationship with significantly different fitting constants, C = 305±10 S/cm and E~O = -0.02±0.005 eV. Of particular significance is the negative value of E~O. A positive value of E~O derives from a movement of the Fermi level by doping up to, but not deeply into the band-tail DOS. Since the same values of E~O apply for a-Si,C:H and a-Si:H, two aspects of their DOSs must be about the same: i) the ratio of the DOS above the band-tail to the DOS in the middle of the gap, and ii) the steepness of the band-tail. For both materials, the activation energy for dark conductivity has not been reduced below about 0.2-0.3 eV by doping, consistent with fundamental limitations in the doping process. In particular, it has not been possible to move the Fermi level deep into the band-tails of a-Si:H by doping because the bonding chemistry of the doping process increases the band-tail DOS. In the statistical shift model, the inverted M-N relation for heavily-doped μc-Si is due to a movement of the Fermi level deep into the band-tail DOS. This interpretation is consistent with a barrier-limited model. In this model, the dark conductivity of heavily-doped μc-Si with activation energies, E~O < 0.1 eV, is by tunneling from occupied conduction (or valence) band states of doped Si crystallites, c-Si, into band-tail states of the a-Si:H that encapsulates the Si crystallites. Under an applied electric field, the Fermi level is moved into the band-tail DOS of the a-Si:H by this tunneling mechanism, so that the inverted M-N rule then applies. Values of C and E~O for these μc-Si samples are in good agreement with the predicted and inverted M-N rule for activation energies, E~O < 0.2 eV [1]. Dark conductivity activation energies > 0.20 eV, and positive values of E~O for doped μc-Si,C result from a non-alignment of conduction (valence) band states of the doped Si-crystallites with band-tail states of the a-Si,C:H that encapsulates these crystallites, thereby preventing direct tunneling deep into the band-tail state distribution. The transport in doped μc-Si,C alloys is by thermionic emission over band offsets between c-Si to a-Si,C:H.

4. Conclusions and Suggestions for Future Research

Research in the area of a-Si,N:H and also a-Si,O:H should be continued. From the research done to date, there are a number properties of a-Si,N:H, prepared by remote PECVD from an N₂ source gas, that are worthy of consideration for treating this alloy as an i-region candidate for the wide bandgap cell in tandem PV device structures. Additional studies are clearly in order, and some of these will be completed before the termination of this program. Samples of a-Si,N:H are being prepared and will be supplied to other team members for studies deemed significant in determining the viability of new candidate PV materials: photocapacitance and SAXS. It is our intention to include these results in the final sub-contract report. We also plan to look at heavily doped Si,O:H and a-Si,N:H as contact materials for TFTs, an application that is similar to PV cell contacts.
Objective and Approach

The initial objective of this research is to investigate the top junctions of hydrogenated amorphous silicon (a-Si:H)-based p-i-n solar cells fabricated by plasma-enhanced chemical vapor deposition (PECVD) in the superstrate configuration [glass/TCO/p-i-n]. Specifically, this means evaluating defects and/or impurities generated when p-type amorphous silicon-carbon alloys (a-SiC:H:B) are deposited onto transparent conducting oxide films (TCO’s), or when intrinsic a-Si:H (or its alloys) are deposited onto a-SiC:H:B layers. As defects are identified and characterized, their influence on the solar cell will be assessed. An additional objective is to utilize these insights to design device preparation/processing for improved performance. A unique capability that will be exploited in this research is real time spectroscopic ellipsometry (RTSE). With RTSE, the layered structure of the device can be measured with sub-monolayer sensitivity. By correlating the observed structure with device measurements, it may be possible to trace the origins of poor device performance to specific interfacial defects at the monolayer level.

Research Results and Discussion

SnO2/a-SiC:H:B Interfaces: Metallic Impurities.

Using RTSE, we have quantified the interfacial metallic contamination that develops when a-SiC:H:B is deposited onto specular, doped SnO2 [1,2]. The free metal at the SnO2/p interface is quantified by its mass thickness, \( d_m \), or volume per area. The mass thickness shows clear variations as a function of the a-SiC:H:B growth parameters. Those that strongly influence \( d_m \) are the gas phase \( H_2 \)-dilution ratio and the substrate temperature \( T_s \); however, the gas phase \( B_2H_6 \) concentration has no discernible effect. For \( T_s=250^\circ \text{C} \) and for a \( H_2 \)-dilution ratio given by \( R=[H_2]/([CH_4]+[SiH_4])=20 \), the mass thickness of free metal that forms at the interface is 5 Å. When \( T_s \) is decreased to 170°C for the same \( H_2 \)-dilution ratio, \( d_m \) is reduced to 2 Å. For \( T_s=250^\circ \text{C} \) and \( R=0 \), no metal can be detected \( (d_m<0.5 \text{ Å}) \), but as \( R \) increases to 2, \( d_m \) increases above the detection limit to 1 Å. From this study, we have determined the deposition parameter space where one must operate to minimize metallic contamination of the SnO2/p interface.

Our ability to determine the mass thickness of free metal by RTSE stems from the fact that, when the metal first forms, it is confined to the SnO2/p interface, where it generates a detectable dielectric discontinuity. Over time scales from days to months at 25°C, however, SE reveals the disappearance of metal from the interface [1]. There are two possibilities that may account for this observation: (i) the free metal may re-oxidize, or (ii) it may diffuse from the SnO2/p interface into the p-i interface region. In the latter case, for example, if a 0.5 Å mass thickness of metal were to diffuse from the SnO2/p interface, dispersing itself throughout a 150 Å thick p-i interface region, an atomic concentration of \( \sim 10^{20} \text{ cm}^{-3} \) would result. Thus, the potential for long-term, irreversible degradation of the solar cell performance is considerable even at the sensitivity limits of RTSE. Now that we have characterized the problem of metallic contamination at the SnO2/p interface, future studies must be devoted to correlating the RTSE characteristics with the performance of co-deposited solar cells.

TCO/a-SiC:H:B Interfaces: Dopant Impurities.

In earlier investigations [3], it was discovered that when an undoped or p-type a-Si:H surface at 200-250°C is exposed to \( B_2H_6/SiH_4 \) gas mixtures in the absence of a plasma, the
B$_2$H$_6$ decomposes on the surface, activating it for subsequent decomposition of SiH$_4$. The net effect is the gradual formation of microstructurally-defective, heavily-doped a-Si:B:H by CVD. For typical gas phase concentrations of B$_2$H$_6$, the CVD material that forms in the multilayer regime contains ~5 at.% B. The initial reaction of B$_2$H$_6$ is very substrate sensitive, and in the earlier work, the reaction was found to be absent on In$_2$O$_3$:Sn (ITO) surfaces. In our recent investigations, we have studied the problem of B$_2$H$_6$ decomposition on specular SnO$_2$ TCO used in solar cell fabrication. This is relevant because, in forming the TCO/p interface of the cell, the B$_2$H$_6$/SiH$_4$ gas mixture is generally allowed to stabilize for a minute or more before plasma ignition. In this time, it is likely that some B$_2$H$_6$ decomposes, contaminating the interface with B. In our recent work, we have found a very slow CVD process (0.03 Å/min) when SnO$_2$ is exposed to the gas mixture used for p-type a-SiC:H:B (CH$_4$:SiH$_4$:H$_2$:B$_2$H$_6$=4:6:1:0.01, in sccm). Thus, in the minute during which the p-type gas mixture stabilizes prior to plasma ignition, no more than 0.01 monolayer of B forms at the SnO$_2$/p interface. In light of possible metallic contamination at this interface, as well, we expect that this low level of B contamination is not a limiting factor in the performance of the cell. This conclusion cannot yet be applied to the ZnO/p interface, and further basic studies are needed for this TCO (see next part).

ZnO/a-SiC:H:B Interfaces: ZnO Modification.

In contrast to the results described above for SnO$_2$/a-SiC:H:B interfaces, no free metal (Zn) is detected by RTSE upon ZnO/a-SiC:H:B interface formation, even under the high H$_2$-dilution conditions that lead to µc-Si:H/a-SiC:H two-phase materials (R=80) [1,2]. Although free Zn is not detected, changes in the optical properties of the near-surface of ZnO are observed upon interface formation. The changes can be interpreted as an increase in the optical gap by ~0.05-0.1 eV, that arises from a shift in the near-interface Fermi level deeper into the ZnO conduction band. The electrical change is caused for the most part by the penetration of H up to 300 Å into the ZnO due to plasma exposure during the nucleation of a-SiC:H:B. We estimate that n-type point defects such as Zn interstitials or O vacancies are created at the level of 0.1-1% of the incorporated H atoms [4]. One might expect an increase in near-interface electron concentration in ZnO to improve hole transport across the junction; however, the actual effect is complex, depending on the nature of the contact and the near-interface density of states in ZnO below the conduction band edge. Further studies in the cell configuration are planned. Other experiments are also needed in order to separate the effects of H and B diffusion into the ZnO, since B can act as an n-type dopant and also enhance the near-interface electron concentration.

p/i Interfaces.

We have quantified the B-contamination that occurs via CVD in the formation of the p-i interface. This effect is expected to be important in solar cell preparation because B$_2$H$_6$ will decompose on the p-layer surface in the time between extinguishing the p-layer plasma and evacuating the gas [3]. As will be noted below, however, the CVD effect continues even while flushing the chamber with an inert gas (after the p-layer gas is evacuated from the chamber). Thus, it appears that the B$_2$H$_6$ is adsorbed on the chamber walls and desorbs during the flushing process. One can also conclude that even if deposition of the p and i layers is performed in separate chambers, significant CVD material may still form after p-layer deposition, during evacuation and transfer. The rate at which CVD growth occurs during exposure of the a-SiC:H:B to the p-type gas (CH$_4$:SiH$_4$:H$_2$:B$_2$H$_6$=4:6:1:0.01, in sccm) is ~0.5 Å/min. The Tauc optical gap of the CVD material, obtained on a 20 Å thick layer is ~1.45 eV, or 0.4 eV lower than the a-SiC:H:B. Such a thin, narrow-gap material at the p-i interface is expected to reduce the open-circuit voltage of the cell; however, the magnitude of the problem is an extremely sensitive function of the preparation procedure (see below).

Baseline Solar Cells: Multi-Chamber System.

In a first attempt, a 7.7% efficient solar cell has been prepared in our multi-chamber system. It has shown the following characteristics: fill-factor, 0.72; open-circuit voltage, 0.82 V; and short-circuit current, 13.1 mA/cm$^2$. The TCO was textured SnO$_2$, and the p-layer was 200 Å.
thick a-SiC:H:B with a band gap of 1.85 eV. No H2 dilution was used in the preparation of the p-layer. The i-layer was prepared to 0.6 µm using conventional a-Si:H growth conditions, and the n-layer was 300 Å thick. No special procedures were performed at the TCO/p and p/i interfaces; thus, this cell is considered a "baseline" mid-gap cell. In the future, we intend to explore the effects of a number of growth parameters/procedures on the characteristics of this cell. These include studies of the effects of the following: (i) varying levels of H2 dilution of the p-layer gas, designed to generate interfacial free metal layers of different d_m; (ii) undoped a-SiC:H buffer layers at the p/i interface, deposited continuously after the p-layer in order to avoid CVD B-contamination; (iii) p-layers prepared by B(CH3)3, also to avoid CVD; and (iv) filament-generated atomic H-treatment at p/i interface to passivate defects.

Baseline Solar Cells: One-Chamber System.

The single-chamber system employed in this research is configured to allow monitoring of solar cell preparation by RTSE. At present only p- and i-layer deposition capabilities exist, so the device is completed with a μc-Si:H n-layer prepared in the multi-chamber system. A μc-Si:H:P layer is deposited at the back of the cell to eliminate any atmospheric contaminants through the etching that occurs in the initial nucleation of the crystallites. In our study of TCO/p/i preparation, we employ three types of substrates: specular SnO2- and ZnO-coated glass for solar cells, and SnO2-coated Si for RTSE. This latter structure is used to enhance the sensitivity of RTSE. The assumption in these studies is that the growth and interface characteristics of a-SiC:H:B are the same for SnO2/glass and SnO2/c-Si structures.

Figure 1(a) shows microstructural data that characterizes a-SiC:H:B growth on SnO2, as determined by RTSE during solar cell preparation. No metal or dopant contamination is detected at the SnO2/p interface for this run, since minimal H2 dilution is used (R=0.1) and the plasma is ignited <1 min after introduction of the p-layer gas. Because the SnO2 surface has an estimated 92 Å of microscopic roughness, a three-layer structure for the a-SiC:H:B film is needed to model the RTSE data. The layers include: (i) an interface roughness layer with a fixed thickness (d_i) of 92 Å, (ii) an a-SiC:H:B bulk layer (thickness: d_b), and (iii) a substrate-induced roughness layer on the a-SiC:H:B surface (thickness: d_s) [see Fig. 1(b)]. In Figs. 1(a) and (b), three regimes are identified: (1) prior to plasma ignition; (2) after plasma ignition but prior to bulk layer formation, and (3) after bulk layer formation. In regime (2), the voids in the SnO2 roughness layer fill with a-SiC:H:B (volume fraction: f) to form the interface layer, and the surface roughness layer develops as the a-SiC:H:B covers the SnO2 conformally. In regime (3), the interface layer has stabilized, the bulk layer develops and increases in thickness linearly with time, and the substrate-generated surface roughness on the a-SiC:H:B smoothen versus time. When the plasma is extinguished, d_i=92 Å, d_b=156 Å, d_s= 66 Å. Figure 2 shows the ellipsometric (ϕ, Δ) trajectory at 2.52 eV during formation of the p/i interface. First, the p-layer plasma is extinguished, and the (CH4/SiH4/H2/B2H6) gas mixture is evacuated and replaced with Ar flushing gas. During this process, and during 55 min of flushing and i-layer gas stabilization, a 25 Å CVD layer forms on the surface of the p-layer. This B-contamination is buried at the interface when the i-layer is deposited. Characterization of the solar cells deposited on the both ZnO and SnO2 TCO's in this run yield identical performances with efficiencies of ~5%. This result suggests that the TCO/p interface is not limiting the cell performance; however, the contamination observed by RTSE at the p/i interface may play a key role. Future efforts will be devoted to correlating the RTSE characteristics of the interface with the cell performance. Buffer layers and p-layer growth using B(CH3)3 dopant gas will both be explored.

References

Microstructural evolution for p-type a-SiC:H growth on specular SnO₂. A three-layer model for the a-SiC:H:B film is required to interpret the RTSE data. This model consists of (i) a fixed-thickness ($d_l = 92 \text{ Å}$) interface roughness layer that develops from the SnO₂ surface roughness, (ii) a bulk-density a-SiC:H:B layer (thickness: $d_b$), and (iii) a roughness layer on the a-SiC:H:B (thickness: $d_g$). The SnO₂/a-SiC:H:B interface layer is modeled during regime (2) as a physical mixture of SnO₂ (volume fraction: 0.50), a-SiC:H:B (volume fraction: $f_i$), and void.

Real time ellipsometry ($\psi$, $\Delta$) trajectory obtained at 2.52 eV during formation of the p/i interface for the solar cell deposition of Fig. 1 (in a one-chamber system). Spectra were collected every 1 s as (i) the p-layer deposition was terminated, (ii) the p-type gas ($\text{CH}_4: \text{SiH}_4: \text{H}_2: \text{B}_2\text{H}_6 = 4:6:1:0.01$) was evacuated from the chamber, (iii) the chamber was purged with Ar gas, (iv) the i-layer gas was stabilized, and (v) the plasma was ignited for i-layer growth. During (ii)-(iii) (a total of 55 min), a 25 Å layer of heavily B-contaminated CVD layer with an estimated optical gap of 1.45 eV forms at the p-i interface (arrow).
In 1993 our research has focused on wide bandgap materials, in conjunction with our participation in the wide bandgap team of the Amorphous Silicon Research Project. We have worked primarily on two topics:

- Electroabsorption Measurements and Built-In Potentials in a-Si:H p-i-n solar cells.
- Photocarrier Drift Mobilities in Wide Bandgap Cells

In the following two sections of this document we describe these results in more detail. In addition to these primary topics, we note our recently published work in several areas:

- Electron drift-mobilities in a-Si$_{1-x}$Ge$_x$:H (collaboration with S. Guha, USSC) [1].
- High-field electron transport in a-Si:H (collaboration with J. B. Chevrier and B. Echer, Palaiseau) [2].
- Optical bias effects on transient photoconductivity in a-Si:H (collaboration with D. Han and M. Silver, University of North Carolina) [3, 5].
- Defect relaxation models in a-Si:H (collaboration with H. Branz, NREL) [4, 5].
- Hopping models for high-field transport in a-Si:H (collaboration with R. I. Devlen and J. Tauc, Brown University) [6].

**Electroabsorption and Built-in Potentials**

One possible limitation to the open-circuit voltage $V_{OC}$ which may be achievable in cells with wide bandgap intrinsic layers is the built-in potential $V_{BI}$. $V_{BI}$ is primarily established by the $p^+$ and $n^+$ layers of the cell. The current uncertainty in estimates of $V_{BI}$ does not permit the issue of the role of $V_{BI}$ to be conclusively resolved, and it is thus unclear how productive research on improved doped layers will be relative to research on improving the intrinsic absorber layer.

We decided to reassess the electroabsorption technique pioneered by the Hamakawa group at Osaka University about ten years ago [7]; we have been collaborating in this research with S. Hegedus at IEC. In the electroabsorption method one measures the modulation the intensity of a laser beam passing through the solar cell due to a synchronous modulation of the bias voltage across the cell. We record this signal as a function of DC voltage bias across the cell; examples of such measurements are shown in Fig. 1. Ideally, the extrapolated voltage where the signal has fallen to zero measures $V_{BI}$, since the external and internal voltages then cancel. This occurs near 0.9 V in Fig. 1.

We are conducting a careful study of the statistical and systematic errors in this technique. In practical solar cells we find that the fraction of $V_{BI}$ dropped in the $p^+$ layer complicates
the interpretation of the electroabsorption signal. In particular, because the electrooptical properties of the $p^+$ and $i$ layers are different, and because some of $V_{BI}$ is dropped in the $p^+$ layer, the intercept in Fig. 1 is wavelength dependent and cannot be directly equated to $V_{BI}$. This effect, though slight, is present in Fig. 1, where results with 633 nm and 670 nm are shown.

We are currently working to solve this problem using solar cells prepared at the Institute of Energy Conversion (IEC), Solarex Corp., and United Solar Systems Corp. For the IEC specimen, for which the wavelength-dependence is small, we estimate $V_{BI}$ of about 0.9 V, in broad agreement with the earlier electrical study which estimated $V_{BI}$ of 1.02 V [8]. Both of these estimates suggest that $V_{OC}$ in wide bandgap cells, which has recently passed 1.0 V, may be significantly affected by the small size of $V_{BI}$. We have not concluded our work with the Solarex and USSC specimens.

Carrier Mobilities in $a$-$Si_{1-x}C_x:H$ and $a$-$Si_{1-x}Ge_x:H$

To improve our understanding of the operation of wide bandgap cells we require some knowledge of their electron and hole drift mobilities. In the last year our knowledge of these mobilities has increased enormously. At Syracuse we have measured $a$-$Si_{1-x}C_x:H$ structures prepared at Solarex Corp. and at Penn State University [3,4]. It is now clear that increasing bandgaps using C alloying diminish the electron drift mobility, presumably by broadening of the conduction bandtail. This is found both in our own work and also in very recent measurements at Swansea University on $a$-$Si_{1-x}C_x:H$ from Utrecht University. We do not find a comparable degradation of the hole mobility.

In Fig. 2 we present a survey of the electron and hole drift mobilities for materials of widely varying bandgap. This comparison is for a definite ratio of drift length $L$ and field $E$ of $L/E = 2 \times 10^{-9}$ cm$^2$/V. The electron measurements are at 200 K; hole measurements were at 298 K. Alloying with either Ge (to shrink the bandgap) or C (to increase the bandgap) diminishes the electron drift mobility. On the other hand, we have not been able to establish any clear effect of alloying on the hole mobility.

We look forward to finding out whether wide bandgap materials prepared without carbon (ie. solely by increasing the hydrogen content) are consistent with these trend.

References

Fig. 1: Modulated electroabsorption signal measured as a function of external bias voltage for a p-i-n solar cell prepared at the Institute of Energy Conversion. Results for 2 laser wavelengths are shown. The voltage for which the extrapolated signal is zero is roughly interpretable as the built-in voltage across the cell; this occurs near 0.9 V in the figure.
Fig. 2: Correlation of electron and hole drift mobilities $\mu_D$ with bandgap $E_G$. Electron mobilities (solid symbols) are reported at 200 K. Hole mobilities (open symbols) are reported at 298 K. All values are mobility estimates corresponding to a ratio of drift-length $L$ to electric field $E$ of $L/E = 2 \times 10^{-9}$ cm$^2$/Vs. The symbol shapes indicate the sources for specimens and prior publication: $\bigcirc$ - a-Si$_{1-x}$C$_x$:H from Solarex Corp. [9,10], $\triangledown$ - a-Si$_{1-x}$C$_x$:H from Penn State University [10], $\bigcirc$ - Stuttgart [11], $\square$ - Energy Conversion Devices [1], $\bigtriangleup$ - Utrecht University [12].
Objective and Approach

Our objectives are to (i) modify film growth to improve the properties of a-SiC:H as the high-gap absorber layer in the multijunction solar cell modules, (ii) identify the factors which dominate the electronic properties of the "top junction" of a-Si:H solar cells, i.e., the TCO/p-doped a-SiC:H and p-doped a-SiC:H/undoped a-Si:H interfaces and (iii) deposit p+ µc-Si,C:H as an alternative to improve these interfaces and solar cell performance. We deposit the films by reactive magnetron sputtering (RMS) because the method (i) provides independent control of hydrogen incorporation via the H\textsubscript{2} partial pressure, (ii) has been used in our laboratory to deposit device quality a-Si:H layers, (iii) produces a-SiC:H films with dense microstructure and good electrical properties, and (iv) is an industrially mature process for the mass production of thin film coatings.

Results

Growth and Properties of a-SiC:H

a-Si\textsubscript{1-x}C\textsubscript{x}:H films would be used as the high-gap absorber in the high-performance multijunction module, and optimization of the electronic properties and stability involves the ternary alloy composition\[1\]. The hydrogen content was found to dominate the increase in the bandgap; increased C content only appears to raise the solubility of the structure for hydrogen. Figure 1 shows the result: the increase of optical gap is linearly related to the increased H content. Also shown are the values for several a-Si\textsubscript{1-x}C\textsubscript{x}:H films grown by PECVD at Solarex and analyzed as part of the NREL wide bandgap team effort. The intrinsic PECVD films obey the same trend as our RMS films, and the doped films have slightly smaller bandgaps. The detailed explanation is likely to be more complex, since C is expected to modify the near-gap density of states. Conflicting claims and data exist in the literature concerning the relation between film composition and the bandgap increase\[2\]; our study has the advantage that both the C and H contents have been accurately measured, and that the growth was carried out at a constant temperature.

Table I shows the results of a-Si\textsubscript{1-x}C\textsubscript{x}:H films with the same composition (x = 17±2 at. % and [H] = 23.0 ± 2.1 at.%) deposited at different temperatures. The Tauc gap is 1.9 eV, the best quality films are grown in the temperature range from 230-310°C. These trends are sharply different from those observed in PECVD a-Si\textsubscript{1-x}C\textsubscript{x}:H films\[3\]. We believe that the difference is due to compositional effects: the PECVD films were reported to have higher carbon content at high temperature.

Solid Source p-type Doping

We have deposited p-type a-Si,C:H films using a powder pressed Si target containing 1 atomic % B. As P\textsubscript{H2} varies from 0.4 to 1.5 mT with T\textsubscript{S} = 230°C and P\textsubscript{CH4} = 0.1 mT, the optical bandgap increases from 1.72 to 1.85 eV and the dark conductivity varies from 2 to 7 ×10\textsuperscript{-7}/Ω-cm. The thermal activation energy for all these films is an impressively low ~ 0.31 eV, measured between 40 and 150°C; at higher temperatures, the activation energy is closer to 0.4 eV. These values compare very favorably with industrial results, eg., from Solarex.
absorption spectroscopy reveals no detectable B-H bonds in these p+ a-Si,C:H films, but we observe the Si-B stretching mode around 700 cm⁻¹. We know from SIMS measurements that the B content is close to that of the target, ~ 1 at. %. The H content is 28 at% from thermal evolution measurements.

We have also deposited p+ µc-Si:H from a powder pressed Si target containing 2.5 atomic % B with hydrogen pressure from 20 to 40 mTorr. The dark conductivity of 0.4/Ω-cm was achieved with bandgap of 1.78 eV and conductivity activation energy of 0.2 eV.

µc-SiC:H Growth

We have deposited microcrystalline SiC alloy films (µc-Si,C:H) as a possible replacement for a-Si,C:H in the p-type contact. In general, the addition of methane (presence of carbon) inhibits µc-phase formation. We increased the hydrogen partial pressure from the 5-8 mTorr used for µc-Si:H growth to 30 mTorr. The resulting hydrogenated silicon carbon alloy film had a significant amount of microcrystalline silicon component, presumably in a matrix of a-Si,C:H. XRD measurement shows strong microcrystalline silicon diffraction peaks (111), (200) and (311), and preferential (111) orientation both on c-Si and Al substrates. However, no crystalline SiC component was found. The dark conductivity is 2.3×10⁻⁷/Ω-cm, about five orders of magnitude higher than in typical a-Si,C:H films.

Nucleation and Growth of µc-Si:H

We deposited µc-Si:H on ZnO substrates by RMS as a precursor study to the growth of p+ µc-Si,C:H on ZnO for the top contact in multijunction solar cells. No chemical reduction is found, but the initial film has a far larger coalescence thickness (~ 100 Å) than for growth on c-Si substrates. This indicates that the ZnO surface condition plays a critical role in microcrystalline nucleation. Figure 2 shows the real time ellipsometry trajectories recorded at a photon energy of 4.5 eV. Chemical reduction produces a kink in the early portion of the ellipsometry trajectory because of the sharply different dielectric function of free metal. The insert shows such a kink for the deposition of a-Si:H on SnO₂ substrates; the reduction was verified by ex situ XPS analysis[4]. However, no reduction was observed for growth on ZnO substrates under any conditions, including very high hydrogen pressures.

The nucleation and growth of µc-Si:H on a-Si:H, which is important for the doped junctions between the p-i-n cells, was analyzed by spectroscopic ellipsometry. We found the first clear evidence for a sub-surface reaction in which µc-Si:H transforms ~ 50 Å of the a-Si:H into µc-Si:H. Figure 3 shows the thickness of these layers as a function of time. The “substrate” is an a-Si:H film of 20 at. % H content; at time t = 0 the hydrogen pressure in the plasma is increased to 5.3 mTorr, which produces µc-Si:H in steady-state growth. Over the first four minutes, we observe the growth of an a-Si:H layer with 24 at. % hydrogen content at a constant rate of 16 Å/min. µc-Si:H begins to appear after 4 minutes of deposition. The dashed line is the total thickness of the high CH a-Si:H plus the µc-Si:H layers; it increases linearly with the same slope before and after µc-Si:H layer formation. The interesting and crucial point in Figure 3 is that the high CH a-Si:H interface layer thickness actually decreases by ~ 40 Å with subsequent µc-Si:H deposition. This indicates that a-Si:H transforms into µc-Si:H in a sub-surface region after µc-Si:H has nucleated at the top surface. We find no evidence for the role of etching in µc-Si:H formation by RMS: if a-Si:H were etched away in-between the µc-Si:H nucleation sites, then we would expect increased values of the void content in the µc-Si:H layer and a lower net growth rate, neither of which is observed.
Conclusion and Future work

The results here clearly demonstrate the potential of (i) reactive magnetron sputtering to improve undoped high gap alloys and (ii) spectroscopic ellipsometry, XPS to study interface formation. In situ Kelvin probe and IR reflectance studies of a-Si,C:H film growth are in progress.

Reference


Table I. Properties of a-Si$_{1-x}$C$_x$:H as a function of substrate temperature.

<table>
<thead>
<tr>
<th>ID</th>
<th>$T_s$ (°C)</th>
<th>$P_{H_2}$ (mTorr)</th>
<th>$E_U$ (meV)</th>
<th>$\alpha_{1.2}$</th>
<th>$\sigma_{ph}$ (1/Ωcm)</th>
<th>$\sigma_D$ (1/Ωcm)</th>
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<tr>
<td>A</td>
<td>150</td>
<td>0.28</td>
<td>71</td>
<td>3.40</td>
<td>1.5E-7</td>
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<tr>
<td>B</td>
<td>190</td>
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<td>64</td>
<td>0.74</td>
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<td>E</td>
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Fig. 1 The optical energy gap for RMS a-Si$_{1-x}$C$_x$:H films vs. the H content; the carbon fraction $x$ is given for each film. Also shown are the values for several a-Si$_{1-x}$C$_x$:H films grown by PECVD at Solarex and analyzed as part of the NREL wide bandgap team activity. The bandgap of all the intrinsic films increases linearly, indicating that the H content may be regarded as the dominant parameter.
Fig. 2  Evidence for TCO reduction from in situ ellipsometry. Inset: optical trajectory for 2 min. deposition of a-Si:H on SnO\textsubscript{2} at P\textsubscript{H\textsubscript{2}} = 0.8 mTorr; the sharp decrease in \( <\varepsilon_1> \) reveals metallic tin at the interface. Main figure: trajectories of a-Si, a-Si:H, and \( \mu\text{c-Si:H} \) films deposited onto ZnO substrates. No ZnO reduction is found for any hydrogen pressure. The best fit curve from optical modelling is plotted along with each data set.

Fig. 3 Nucleation and growth of \( \mu\text{c-Si:H} \) on a-Si:H deduced from spectroscopic ellipsometry and modelling. Initially, a high hydrogen content a-Si:H layer forms; then a \( \mu\text{c-Si:H} \) layer nucleates and consumes \( \sim 40 \) Å of the a-Si:H in a sub-surface phase transformation. The dashed line is the linear fit to the total thickness of both layers; there is no change in the deposition rate as a function of the surface phase. Solid lines are guides to the eye.
The objectives of our research were (1) to determine how recombination, trapping and band mobility modifications affecting the electronic properties of amorphous semiconductors can be characterized and described by an appropriate spectrum of defect states, (2) how light induced defects (SWE) in a-Si:H and native defects in a-Si:Ge:H affect the transport properties in these materials.

Experimentally we focused on electroluminescence (EL), and transient forward bias current (TFBC) as a function of device parameters such as thickness of the i-layer and p-i junction properties before and after photo-degradation. The samples were obtained through a collaboration with Y.M. Li at SOLAREX, S. Hegedus at IEC, J.P. Xi at APS and Dick Crandall at NREL. The sample preparation conditions and cell performance are listed in table I. The i-layer thickness of the p-i-n devices varied from 0.2 µm to 10 µm.

**Buffer-layer Dependence of EL Spectra**

EL is a result of radiative recombination both in the bulk and in the junction region. As noted last year, in 0.4 µm cells with buffered layer, p-b-i-n's, the main band (1.2 eV) luminescence was more pronounced than in simple p-i-n's.\(^1,2\) Those samples were made by dc PECVD at Solarex. This year we measured 0.5 µm p-b-i-n and p-i-n samples made by photo CVD at IEC, University of Delaware. Fig. 1a shows the light-soaking effect on EL spectra in p-b-i-n and p-i-n solar cells made at IEC. The p-b-i-n samples show more pronounced high energy EL band than the p-i-n samples and almost the same as the Solarex's samples, although the EL spectrum-line-shape is

![EL spectra and SWE in 0.5 µm p-b-i-n and p-i-n cells at 300 K under 0.9 V.](image1.png)

The open circles indicate original state A, the triangles indicate light-soaked state B.

![EL spectra and SWE in 0.5 µm low- and high- H content cells at 300 K under 0.9 V.](image2.png)

The open circles indicate original state A, the triangles indicate light-soaked state B.
varied depending on deposition conditions. (Perhaps the more pronounced main band emission is related with improved open circuit voltage, \( V_{oc} \), as seen in table I.) However, we found a greater decrease of the 1.2 eV EL band in p-b-i-n than in p-i-n cells after light-soaking. While the most SWE was found in 11 at % H-content cells without buffer-layer as shown in Fig. 1b.

**i-layer Thickness Dependence of EL Spectra**

The EL was dominated by the 1.2 eV main band emission for the samples with thicknesses of 0.2 µm - 10 µm at \( T < 150 \) K. With increasing temperature, there is a shift toward low energy luminescence (~ 0.9 eV) in all samples as found in PL. However, thicker samples (≥ 0.2 µm) show significantly more main band emission (~ 1.2 eV) than thin samples.\(^3\) The EL spectra of the 0.2 µm sample show the lowest peak energy at 300 K. These results suggest to us that the "defect" luminescence dominates near the junction (probably at the p-i region) while the "main" band luminescence dominates in the bulk. One expects the density of defects to be higher near the junction region than in the bulk. The fraction of the volume occupied by the junction region is large in thin samples, and the "defect" emission dominates. Figure 2a shows the thickness dependence of EL spectra at 300 K. The thin samples show more "defect" while the thicker samples show more "main" band luminescence. Figure 2b shows the thickness dependence of EL spectra at 200 K for the same group of samples as in figure 2a. Notice that, first the EL peak energy shift to higher energy is more obvious as the thickness increases from 0.2 µm to 10 µm; second, the EL spectrum of the 0.2 µm sample shows a high energy 1.2 eV emission peak. The latter may originate from the higher electrical field across the i-layer.

![Fig. 2a Thickness dependence of EL spectra at 300 K. Fig. 2b Thickness dependence of EL spectra at 200 K.](image)

**Applied Voltage Dependence of EL Spectra**

The applied voltage dependence of EL spectra has been observed in thin and thick p-i-n samples.\(^3\) The common feature is that under high electrical field the EL spectrum contains a larger fraction of "main" band emission while under low electrical field the EL spectrum shows a larger fraction of the "defect" emission. Figs 3a and 3b show the results for a 0.2 µm p-i-n and 2.0 µm p-i-n at 300 K. These results suggest that either the carriers re-distributed among the localized states (tail states and gap states) or the "defect relaxation" takes place when the non-equilibrium carrier's concentration increased.
Light-soaking effect on EL decay

We have found that the lifetime distribution in thin samples peaks at $10^{-6}$ sec in the temperature range of 80 K - 300 K while in thick samples at $T < 250$ K the lifetime distribution is double peaked at $10^{-6}$ sec and at $10^{-3}$ sec. We have further studied the light-soaking effect on EL lifetime distribution in thin 0.4 µm p-i-n. As shown in Fig. 4a the EL signal delay is longer and decay is much slower in light-soaked state B than in annealed state A. This perhaps implies a broad distribution of lifetimes in state B as shown in Fig. 4b.

Transient Forward Bias Current in p-i-n

The general feature of transient forward bias current is a decaying initial space-charge-limited current followed by a delayed rise of recombination current. No fast-trapping processes of the current transient in either n-i-n or p-i-n have been found. Moreover, a relaxation time as long as $10^4$ sec was observed after injecting carriers in p-i-n samples. Further, the transient current in p-i-n shows a Negative Bias Effect. This effect in thin (0.2-0.5 µm) p-i-n’s can be understood by a junction depletion effect. However, we found a much larger negative bias effect in thick
(2-10 µm) p-i-n and n-i-p samples. So far no computer simulation can fit with these experimental curves.\(^4\) Clearly, a new mechanism, besides the parameters we have known, must be involved.

**Future Study**

Our results of EL spectra dependence of buffered-, non-buffered cells and i-layer thickness indicate that there is a correlation between the cell performance and the recombination mechanism. Future work will focus on:

1. Comparison study of EL and TFBC in high-performance cells as a function of device structure or technology, such as single- or multi- a-Si:H/a-Si:Ge:H junction (ECD), pure silane or H-diluted silane deposition (SOLAREX), low SWE cells (APS) etc.
2. Light-soaking effect on EL spectra and EL decay of the above samples.
3. How recombination modification and SWE defects affect the electronic properties of the materials and the device parameters.

**References**

2. Electroluminescence and forward bias current in p-i-n and p-b-i-n a-Si:H solar cells, Keda Wang, M. Silver, and Daxing Han, J. Appl. Phys. 73 (1993) 4567.
4. Private communication with M. Hack.

<table>
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Title: Microscopic Origins of Metastable Effects in a-Si:H and Deep Defect Characterization in a-Si,Ge:H Alloys

Organization: University of Oregon, Eugene, Oregon

Contributors: J. David Cohen, Principal Investigator; John Hautala, Thomas Unold, and Fan Zhong

The primary goals of this program are to investigate the mechanisms by which a-Si:H degrades with light exposure and to elucidate the defect structure in the low bandgap a-Si,Ge:H alloys. During the past year we have made major progress in our efforts to understand key factors affecting the deep defect densities in the low bandgap alloys and our report below summarizes these findings. We have also carried out more detailed studies of the effects of light-induced degradation on carrier trapping dynamics in pure a-Si:H samples.

Approach and Results

Samples for the studies reported below were obtained from a variety of sources. The glow discharge a-Si:H was grown in-house, the photo-CVD a-Si:H and a-Si,Ge:H alloys were obtained from the Institute for Energy Conversion, and the glow discharge a-Si,Ge:H samples were obtained from S. Guha at U.S.S.C. All films were at least one micron thick and were deposited on p+ crystalline Si substrates. A semitransparent Pd Schottky barrier was evaporated on the free surface.

The results described in this report were obtained primarily by two techniques: drive-level capacitance profiling and transient photocapacitance spectroscopy in tandem with transient photocurrent measurements. The first method has been described in detail elsewhere\(^1^,\)\(^2\) and is used to directly determine an integral over the density of mobility gap defect states:

\[
N_{DL}(E_e) \equiv \int_{E_e}^{E_F} g(E) \, dE \quad \text{where} \quad E_e(\omega,T) = k_B T \log(v/\omega). \tag{1}
\]

Here \(E_F^0\) is the bulk Fermi level position in the sample. By altering the measurement temperature (or frequency) we can alter \(E_e\) and thus obtain information about the energy distribution of the defects. By altering the applied DC bias, we can vary the spatial region at which we detect the defects. In Fig. 1 we show an example of such a series of measurements for a USSC a-Si\(_{1-x}\)Ge\(_x\):H sample (\(x=0.35\)) where we can observe a clear upper limit for \(N_{DL}\). This we identify with the total defect density. Thus we obtain a quantitative measurement of the deep defect levels in these samples. In addition, we are able to assess the spatial uniformity of the distribution of these defects.

We can reconstruct the energy distribution of gap states as well. For a particular spatial region (near 0.55\(\mu\)m in Fig. 1) we plot in Fig. 2 the value of \(N_{DL}\) vs. the energy \(E_e\) given by Eq. (3). Then, by differentiating this curve with respect to \(E_e\) [see Eq. (1)] the density of states is obtained directly. In the case of this a-Si,Ge:H sample we obtain a clear picture of a defect band centered at \(E_C - E_e = 0.75\) eV. The variation of the magnitude of this defect with metastable treatment is also shown and indicates a factor of 3 increase in this defect band after 800h of AM1 light exposure.
The methods of junction transient photocapacitance and photocurrent have been discussed by us in great detail over the past several years\textsuperscript{3,4,5,6}. They are both forms of sub-band-gap optical spectroscopy and provide spectra quite similar in appearance to PDS derived sub-band-gap optical absorption spectra. However, instead of detecting absorbed energy, our transient methods detect the optically induced change in defect charge within the depletion region. Unlike the CPM method, our junction based techniques are not greatly influenced by the free carrier mobilities since, once an electron (or hole) is optically excited into the conduction (valence) band it will either totally escape the depletion region on the slow timescale of our measurement (0.1 to 1s) or be retrapped into a deep state and not escape. In general we assume that almost all of the optically excited majority carriers (electrons) do escape but usually only a fraction of the minority carriers (holes).

These sub-band-gap spectroscopies complement the drive-level profiling method because they allow us to examine \( g(E) \) over a much larger energy range but give less quantitative information with much less spatial resolution. Of particular importance is that photocapacitance and photocurrent measurements have different sensitivities to the loss of electrons vs. holes from the depletion region. Thus a detailed comparison of the two kinds of spectra can distinguish whether optical excitation of defect states comes about because of the excitation of trapped electrons to the conduction band or because of the excitation of valence band electrons into an empty mobility gap state. Similarly we can determine the escape length of the holes which then allows us to estimate the hole \( \mu \tau \) products\textsuperscript{5,7} (for a trapping time, \( \tau \)). This ability to distinguish electron from hole processes is unique among all the various types of sub-band-gap optical spectroscopies. Representative results for the USSC a-Si,Ge:H sample of Figs. 1 and 2 are displayed in Fig. 3.
Fig. 3. Two pairs of transient photocapacitance and photocurrent spectra for the U.S.S.C. a-Si,Ge:H sample. The spectra in (a) for 300K are nearly identical due to the suppression of hole motion out of the depletion region. At 350K (b) the spectra differ dramatically because the photocapacitance signal is proportional to the electrons minus the holes that escape while the photocurrent is proportional to the sum.

Discussion

The transient photocapacitance and photocurrent spectra are nearly identical for the 300K measurements due to the suppressed hole motion caused by a low \(\mu n\) at lower temperatures. However, the curves differ dramatically for the 350K measurements, clearly showing the role of hole processes in these optical excitations. A striking aspect is that the photocapacitance signal changes sign slightly near 1.2eV, meaning that the hole current actually exceeds the electron current in this region. As discussed previously\(^5,6\), this signifies the presence of a distinct defect band lying above \(E_F\) from which electron thermal emission is suppressed. This is to be contrasted with the sub-band-gap spectra for a-Si:H which show no such feature\(^4\). Thus there is a significant difference between the deep defect properties of a-Si:H and a-Si,Ge:H. However, both a-Si:H and a-Si,Ge:H do exhibit similar spectral evidence for a defect band near midgap whose magnitude matches that deduced by the drive-level profiling measurements. A summary of the positions of the defect bands deduced for a series of compositions of samples produced by the photo-CVD method is shown in Fig. 4.

The midgap defect densities obtained from the drive-level profiling method is shown in Fig. 5. These data indicate an exponential increase of defect densities with Ge fraction. We have determined\(^7\) that this dependence agrees in detail with a model\(^8\) that predicts that all valence bandtail states that would have existed deeper in the gap than some demarcation energy, \(E^*\), instead become deep defect states. The position of \(E^*\) for each sample is determined directly from the positions and widths of the midgap defect band revealed by the sub-band-gap spectra. Together with the measured value of the Urbach energy, the magnitudes of the defect density is predicted. This prediction is shown by the solid line in Fig. 5 and agrees quite well with the values found by the drive-level capacitance measurements.
Important Issues for Future Study

While a great deal of information concerning the defect structure in a-Si:H and a-Si,Ge:H films has thus been obtained over the last several years through the use of the methods discussed in this report, a great deal of work still remains to be done. We have employed the drive-level profiling method to good advantage in several studies of metastable defect creation in a-Si:H, however, such work has only just begun for the a-Si,Ge:H alloys and must be extended to a much wider composition range. Also, we plan to devote some effort in the near future to actually identifying the defect bands that we have observed in the alloy samples. We also want to apply these methods to a-Si:H samples produced by other deposition methods and to samples containing varying amounts (or types) of hydrogen. Finally, we are particularly interested in trying to develop the drive-level profiling method for direct application to p-i-n devices so that we can compare our results to the photovoltaic performance.

References

The aim of this research project is to improve the performance of a-Si:H-based solar cells through the understanding of metastability, doping and growth.

**Deposition properties of a-Si:C:H alloys**

Studies of wide gap alloys have begun, in accordance with the recent restructuring of the NREL program. We are making a systematic study of the deposition parameters that lead to high-quality undoped a-SiC:H alloys. Initially we are using ESR to characterize the defect density and optical absorption to obtain the band gap, and have made comparisons with Solarex material. The growth parameters studied are H dilution, CH₄ concentration, temperature and power and a selection of data is shown in Figure 1. For our 2eV gap a-SiC:H films we have obtained similar properties, in particular the spin density of our films is ~1.5x10¹⁷ cm⁻³ in comparison to 3x10¹⁷ cm⁻³ on the benchmark Solarex samples. Our results on samples deposited with high hydrogen dilution, high rf-power, and a moderate CH₄/SiH₄ ratio indicate that the bandgap can be pushed above 2.2eV without significant increase in defect density. For a fixed ratio of CH₄/SiH₄ the bandgap can be shifted from 1.9eV to 2.2eV by hydrogen dilution alone. A non-monotonic dependence of defect density on hydrogen dilution is observed. While for dilutions below 90% an increase in the defect density is found, higher dilutions reduce the

![Figure 1. Plot of ESR spin density versus band gap for a-Si:C:H samples deposited at different hydrogen gas dilution.](image-url)
defect density, leading to 2.2eV bandgap films with the same defect density as the 1.9eV gap films. The increase in bandgap at the high H-dilution regime is accompanied by an increase in the carbon concentration, from 3.4% to 4.5% for gaps from 2.0eV to 2.1eV, while the hydrogen concentration stays essentially constant at 20%, suggesting preferential etching of weak Si-bonds from the growing surface as the mechanism responsible for improving the film quality and at the same time increasing the bandgap.

Metastability in polysilicon

In order to understand better the origin of metastable defects in a-Si:H we have studied hydrogenated polycrystalline silicon films. Films were deposited by low-pressure chemical vapor deposition and were exposed to monatomic hydrogen to passivate grain boundary defects. The spin density was measured before and after illumination and for the first time the light-induced creation of paramagnetic defects in hydrogenated polycrystalline silicon has been observed, as shown in Figure 2. The ESR spectrum was the same as observed in a-Si:H and is interpreted as grain boundary silicon dangling bonds with a random distribution of orientations. The light-induced defect creation in poly-Si:H was measured for various temperatures and exhibits the same weak temperature dependence as in a-Si:H. These data strongly suggest that the source of new metastable dangling bonds in poly-Si:H are weak Si-Si bonds, as in a-Si:H, and the defect creation mechanism in both materials is similar.

\[
N_S \text{ (cm}^{-3}\text{)}
\]

![Figure 2. Plot of the ESR spin density for undoped LPCVD poly-silicon films. The initial state (squares) occurs after hydrogenation at 350°C; open triangles are after annealing at 160°C; closed triangles are after light soaking.](image)

The poly-Si:H films were light soaked and annealed several times as indicated in Figure 2. An anneal at 160°C restored the initial state only during the first 2 cycles, but further cycles weaken the effect. \(N_S\) in the annealed state increases, and the spin density in the light soaked state B decreases. The samples again were exposed to monatomic hydrogen at 350°C for 60 min. followed by an anneal at 160°C which led to a full recovery of the light-induced defect creation process. This result can be
explained only by assuming that hydrogen is involved in metastable defect creation. The ability to rejuvenate the metastability simply by re-exposure to monatomic hydrogen clearly establishes the participation of hydrogen in the phenomenon. Since the effect is qualitatively and even quantitatively identical in poly-Si:H and a-Si:H, the results strongly support the view that hydrogen is directly involved in the light-induced metastability in a-Si:H as well.

Hall effect measurements on a-Si:H and a-Si:C:H

We have performed Hall effect measurements on a-Si:H and a-Si:C:H over a broad temperature range (200-400K), to see if the technique can be used to gain more information about the properties of free carrier transport, despite the anomalous sign. The experiments correlate the Hall measurements with sweep-out, conductivity and thermal quenching. Quenching allows a reversible variation of the band tail carrier density, n_BT, whereas variable temperature measurements change the drift mobility while keeping n_BT constant.

![Figure 3. Hall mobility, µ_H, conductivity, σ, and Hall carrier density, n_H, measured as a function of temperature in n-type a-Si:H.](image)

The electron Hall mobility, µ_H, is approximately independent of temperature, and varies with doping from a high of 0.15 cm²/Vs in intrinsic a-Si:H to a low of 0.05 cm²/Vs in 1% doped a-Si:H. The µ_H of holes is smaller than for electrons. µ_H is also independent of n_BT, as is shown by thermal quenching measurements. The Hall mobility of undoped material was obtained by illumination to give excess free carriers, because the samples are too resistive in the dark. Illumination causes a magneto-resistance effect which must be subtracted off to get the Hall coefficient. Measurements were also made on n-type alloys of a-Si:H with C, made with gas-phase CH₄ concentrations ranging up to 75%. Increasing the carbon concentration leads to a continuous decrease of µ_H with a significant drop by about a factor 5 for C contents larger 50%. The decrease in µ_H occurs at the same carbon concentrations.
where the conductivity decreases by 2-4 orders of magnitude, which is interpreted in terms of a rapid widening of the band tails.

The new results continue to support the model that $\mu_H$ is a constant fraction of the free mobility ($\mu_H \sim \mu_0/100$). Confirmation of this relation would allow an convenient determination of free mobilities and carrier densities based on Hall experiments. We speculate that the reduced Hall mobility observed in p-type material and in the a-Si:C alloys are both due to increased disorder, and are closely correlated with the wider distribution of band tail states.

**Defect creation and hydrogen diffusion**

Light induced hydrogen diffusion provides a direct link between defect creation and hydrogen motion. To explain the temperature dependences of defect creation, light induced hydrogen diffusion and recombination induced defect recovery, we propose a mechanism which combines both a thermal and a carrier-induced mechanism to break a Si-H bond. At sufficiently low temperatures metastable defects are created solely by the recombination energy. However, thermal excitations may also contribute at elevated temperatures. The thermal excitation process involves the simultaneous excitation of many phonons at an Si-H bond with probability $\omega \exp(-E/kT)$. The carrier enhancement mechanism is believed to result from a multiphonon recombination of electrons and/or holes. In either case, the total phonon excitation needs to be large enough to overcome the barrier, $E_B$, to release hydrogen from an Si-H bond. In the combined mechanism, part of the energy, $E_{th}$, comes from thermal excitation and a part, $E_R$, comes from carrier recombination.

After the recombination event has created a multiphonon excitation, the energy is dissipated very rapidly by inelastic phonon scattering and spreads over an increasingly large volume, so that low energy excitations have the highest probability. The rate of loss of energy is expected to be temperature independent, and therefore we use an empirical model in which the probability of an excitation of energy $E_R$ is, $G_R \exp(-E_R/E_X)$, where $G_R$ is the recombination rate (per H atom) and $E_X$ is a parameter describing the rate of energy loss. A calculation shows that at room temperature the recombination enhanced bond breaking rate has a weak temperature dependence because the excitation is almost completely due to carrier recombination. In contrast, thermal excitation provides most of the energy at high temperature and the rate increases due to the high probability of low energy excitations. The model shows that the recombination induced effect is greatly enhanced when the thermal excitation rate is significant.

**Bibliography**

5.0 PHOTOVOLTAIC MANUFACTURING TECHNOLOGY (PVMaT) PROJECT

Ed Witt, (Manager)

The Photovoltaic Manufacturing Technology (PVMaT) Project is a government/industry PV manufacturing research and development (R&D) project composed of partnerships between the federal government (through DOE) and members of the U.S. PV industry. It is designed to assist the U.S. PV industry in improving manufacturing processes, accelerating manufacturing cost reductions for PV modules, increasing commercial product performance, and generally laying the groundwork for a substantial scaleup of U.S.-based PV manufacturing plant capabilities.

The project is being carried out in three separate phases, each focused on a specific approach to solving the problems identified by the industrial participants. These participants are selected through competitive procurements. Furthermore, the PVMaT project has been specifically structured to ensure that these PV manufacturing R&D subcontract awards are selected with no intention to either direct funding toward specific PV technologies (e.g., a-Si, polycrystalline thin films, etc.) or to spread the awards among a number of technologies (e.g., only one subcontract in each area). Each associated subcontract under any phase of this project is, and will continue to be, selected for funding on its own technical and cost merits.

The Phase 1 portion of the PVMaT program, the problem identification phase, was completed early in 1991. This solicitation was open to any U.S. firm with existing PV manufacturing capabilities, regardless of material or module design. Early in 1991 the competitive selection process for this phase was completed with contracts being awarded to 22 of approximately 40 offerors. Each of these subcontracted efforts was funded at a level of up to $50,000 and a duration of 3 months. Problems identified by the research in this phase of the program were primarily process-specific in nature and represented opportunities for individual industrial participants to improve their manufacturing processes, reduce manufacturing costs, increase product performance, and/or support a scaleup of U.S.-based manufacturing plant capabilities. These opportunities have since been detailed in the approaches suggested by these organizations for Phase 2 R&D. It is not anticipated that any additional Phase 1-type solicitation will be issued, as the Phase 1 was intended to develop initial problem and manufacturing status information and to support the PV industry in preparing for later PVMaT problem solution phases.

Phase 2, the problem solution phase that addresses process-specific problems of specific manufacturers, is now under way with an expected duration of 5-years. The first solicitation under this phase (PVMaT 2A) was open only to those organizations that received awards in the Phase 1 solicitation, and seven resulting subcontracts were implemented in early 1992. The subcontracts are cost-shared between the U.S. government and U.S. industrial participants. Technical accomplishments for the first year of PVMaT 2A are presented below. Proposals for a second, overlapping, and similar process-specific solicitation (PVMaT 2B) were received in September of 1992. This second Phase 2 solicitation is in the evaluation stage with awards planned for early FY.1994. PVMaT 2B was open to all U.S. PV industrial firms, thus giving organizations that were not ready for the first Phase 2 procurement cycle another chance to "ramp
on" and participate in the solution phase of the program.

Phase 3 addresses R&D problems that are relatively common to a number of PV companies or the PV industry as a whole. These "generic" problem areas are being addressed through a teemed research approach. A solicitation (Phase 3A) for these teemed research efforts was released in October 1991. Two subcontracts for Phase 3A were awarded early this year. These research organizations are focusing on module-related R&D problems found to be common to a significant set of PV manufacturers and these subcontract activities are described below.

RECENT PROGRESS

Phase 2A

The winners in PVMaT 2A are listed in the Table 2 below. Following Table 2 is a description of the two subcontractor projects and their first year PVMaT accomplishments.

Table 2: PVMaT Phase 2A Participants

<table>
<thead>
<tr>
<th>Subcontractor</th>
<th>Subcontract Title</th>
<th>Principal Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siemens Solar Industries</td>
<td>Photovoltaic Cz Silicon Manufacturing Technology Improvements</td>
<td>T. Jester</td>
</tr>
<tr>
<td>Camarillo, California</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solarex Corporation</td>
<td>Large-Area, Triple-Junction, a-Si Alloy Production Scale-Up Project</td>
<td>R. Oswald</td>
</tr>
<tr>
<td>Newtown, Pennsylvania</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mobil Solar Energy Corporation</td>
<td>Thin Edge-Defined Film-Fed Growth (EFG) Octagons</td>
<td>J. Kalejs</td>
</tr>
<tr>
<td>Billerica, Massachusetts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ENTECH, Inc.</td>
<td>Photovoltaic Manufacturing Technology (PVMaT) Improvements for ENTECH's Concentrator Module</td>
<td>M. O'Neill</td>
</tr>
<tr>
<td>Dallas, Texas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AstroPower, Inc.</td>
<td>Silicon-Film™ Photovoltaic Manufacturing Technology</td>
<td>W. Bottenberg</td>
</tr>
<tr>
<td>Newark, Delaware</td>
<td></td>
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</tr>
<tr>
<td>Utility Power Group</td>
<td>a:Si Photovoltaic Manufacturing Technology—Phase 2A</td>
<td>G. Duran</td>
</tr>
<tr>
<td>Chatsworth, California</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy Conversion Devices</td>
<td>Continuous Roll-to-Roll Amorphous Silicon Photovoltaic Manufacturing Technology</td>
<td>M. Izu</td>
</tr>
<tr>
<td>Troy, Michigan</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Siemens Solar Industries: Photovoltaic Cz Silicon Manufacturing Technology Improvements - Siemens Solar Industries (SSI) is improving Cz Si(c-Si)-ingot quality; increasing the materials use efficiency for c-Si wafer sawing; investigating improvements in device processing; investigating the introduction of automation to a significant portion of its c-Si module manufacturing lines; and reducing the amount of hazardous waste generated. This effort is being addressed in three 1-year phases. Successful implementation of this program will result in
decreasing SSI’s c-Si module cost by more than half while doubling its U.S. manufacturing capability. Siemens's accomplishments during the first phase of this subcontract include an increase in wire-saw production capacity by more than 30% due to reduced Kerf loss and thinner wafer processing; an increase in crystal growth yields through polysilicon studies; use of Freon is being eliminated and replaced by a no-clean solder paste in Siemens module production by April 1993; and incorporation of graphite design changes into the Siemens crystal growers has resulted in a 30% savings of $300K/year.

**Solarex Corporation Large-Area, Triple-Junction, a-Si Alloy Production Scale-Up Project** - The Solarex Corporation is improving the deposition and quality of its transparent front contact; optimizing its laser patterning process; scaling up the semiconductor deposition process; improving the back contact deposition; and scaling up and improving the encapsulation and testing of its a-Si:H modules. Successful implementation of this 3-year program will result in Solarex producing 0.54-m² (≥6ft²), 10% stabilized efficiency, 75-Watt a-Si:H modules with a total overall module yield of ≥75%. At a proposed production capacity of 10 MW/year, this would result in a potential cost reduction from the present price of $11.05/Wp to $1.14/Wp. Solarex's accomplishments during the first phase of this subcontract include the design of a 0.54-m² (≥6ft²) PECVD a-Si:H based deposition system; completion of light soaking tests on Solarex a-Si:H modules; demonstration of a new laser-anscribing system that does not cause module failures in the wet hi-pot tests; and the fabrication of a Frit Dispenser used in Solarex module fabrication.

**Mobil Solar Energy Corporation Thin Edge-Defined Film-Fed Growth (EFG) Octagons** - Mobil Solar Energy Corporation is reducing the cost of solar cell processing through a 50% reduction in its EFG Si-wafer thickness; increasing the throughput of the laser-cutting of the wafers; increasing the mechanical strength and thus yield of the wafers; and evaluating integrated computer-aided manufacturing control programs for the Mobil Solar crystal growth manufacturing line to enhance productivity. Successful implementation of this 3-year program will allow Mobil Solar to produce octagonal Si tubes, producing 200-µm-thick Si wafers with a thickness variation of ±50 µm. The previous minimum wafer thickness for this process was 400 µm. Mobil Solar will also develop laser wafer-cutting capabilities resulting in the processing of 12 wafers per minute. Mobil Solar’s accomplishments during the first phase of this subcontract include testing and analysis that indicate potential materials cost reductions of 15% due to wafer thickness, 10% due to wafer flatness improvement, and 25% due to a growth rate; completing specifications for a factory prototype EFG octagon crystal growth furnace for 300-µm-thick Si wafers; designing and testing a laser cutting station that will increase pilot production line throughput by a factor of two; and demonstration of the cutting feasibility of silicon wafers near the low-damage threshold with a 585-nm high power dye laser.

**ENTECH, Incorporated Photovoltaic Manufacturing Technology Improvements for ENTECH’s Concentrator Module** - ENTECH is automating a significant portion of its manufacturing line, aiding key ENTECH vendors in improving the vendors’ technologies; scaling up the ENTECH manufacturing line to accommodate large volume production; and addressing ES&H issues throughout all of the associated manufacturing processes. The effort is being addressed in two, 1-year phases. Successful implementation of this program will result in an initial linear concentrator module manufacturing plant with the capability of producing PV modules at a rate of 10 MW/year. ENTECH’s accomplishments during the first phase of this subcontract include;
the development of laboratory prototype work stations for PV cell assemblies and receivers; the identification and delivery of process-compatible advanced-cell samples from four separate vendors; the development of an improved prismatic lens cover for cells which resulted in a 90% reduction in both material and labor costs for that step; the development of a continuous, prelaminated, rolled Fresnel lens, which resulted in both a 20% materials cost reduction and the elimination of solvent use in the ENTECH process; and development of ribbon solder techniques that have resulted in an 80% reduction in materials costs with additional savings in labor.

**AstroPower, Incorporated Silicon-Film™ Photovoltaic Manufacturing Technology** - AstroPower is enhancing its Silicon-Film™ wafer production capabilities, optimizing its solar cell processing, and improving the polycrystalline silicon-film module assembly portion of its manufacturing line. Successful implementation of this 3-year program will result in an upgrade to AstroPower's facility that will allow it to reach a production rate of 19 MW/year of 1.22-m² polycrystalline silicon modules with an output of 170 Wp each by the mid-1990s. AstroPower's accomplishments during the first phase of this subcontract include its demonstration an 8.8% efficient 10-cm x 10-cm Silicon-Film™ solar cell; the fabrication of the first 15-cm x 45-cm Silicon-Film™ cell (the largest solar cell ever produced); a demonstration of a 0.48 MW/year Silicon-Film™ machine operation rate, and 74% silicon feedstock use efficiency; the initial planning for 2.4 MW/year wafer fabrication machine; and planning for the introduction of new 225-cm² Silicon-Film™ solar cell product in 1993.

**Utility Power Group a:Si Photovoltaic Manufacturing Technology—Phase 2A** - The Utility Power Group (UPG) is conducting research on encapsulation of its a-Si:H modules, with consideration given to approaches that do not require a second glass layer, and automation of module termination. Additionally, UPG's lower-tier subcontractor, Advanced Photovoltaic Systems (APS), is optimizing the automation of its Eureka manufacturing line; improving the encapsulation of the Eureka module and introducing real-time processing and quality control to the Eureka production line. Successful implementation of this three-year effort will result in increasing the module manufacturing yield over the current level by 35% while decreasing the direct cost by about 25%. The accomplishments of the UPG-APS team during the first phase of this subcontract include the completion of POWERGLASS module qualification testing for candidate encapsulation materials; reduced POWERGLASS module termination and encapsulation manufacturing costs by 50%; the introduction of three new Eureka module products (25-W and 50-W products for 12-Volt applications); completion of the automation of about 60% of the Eureka production encapsulation line; and completion of a design for full-scale enhanced Eureka modules.

**Energy Conversion Devices, Incorporated Continuous Roll-to-Roll Amorphous Silicon Photovoltaic Manufacturing Technology** - Energy Conversion Devices (ECD) is developing the production of 0.3-m x 1.2-m (1-ft x 4-ft) triple-junction a-Si-Ge alloy modules with 11% stable efficiency, reducing its manufacturing costs through utilization of ECD's high deposition rate microwave technology to enhance the production throughput, and reducing material and labor costs. The effort is being addressed in three 1-year phases. Successful implementation of this program will allow ECD to work toward an ultimate goal of building a 100 MW/year roll-to-roll, automated a-Si module manufacturing facility. At this anticipated production capacity, ECD could reduce the cost of PV-generated electricity to less than $1.00/Wp. ECD's accomplishments
during the first phase of this subcontract include completion of improvements to the ECD a-Si-Ge alloy deposition system establishing the first roll-to-roll a-Si-Ge production line facility; demonstration of 7.2% stabilized efficiency on 0.37-m² (24 ft²) triple-junction a-Si alloy modules; and incorporation of a Linear Applicator Microwave Plasma source for multipurpose deposition.

Phase 3A

The winners in PVMaT 3A are listed in the Table 3 below. Both contracts began in early January, 1993.

<table>
<thead>
<tr>
<th>Subcontractor</th>
<th>Subcontract Title</th>
<th>Principal Investigator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spire Corporation</td>
<td>Automated Solar Cell Assembly Teamed Process Research</td>
<td>M. Nowlan</td>
</tr>
<tr>
<td>Bedford, Massachusetts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Springborn Laboratories, Inc.</td>
<td>Photovoltaic Manufacturing Technology (PVMaT)</td>
<td>W. Holley</td>
</tr>
<tr>
<td>Enfield, Connecticut</td>
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</tbody>
</table>

Spire Corporation *Automated Solar Cell Assembly Teamed Process Research* - Spire will conduct manufacturing R&D to improve crystalline and polycrystalline Si PV module manufacturing processes with a goal of substantially reducing module manufacturing costs. Areas that will be addressed include processing rates, process control, yield, throughput, material utilization efficiency, and increased use of automation. These issues are being addressed for thin (≤ 200 µm) silicon wafers. To conduct these efforts, Spire will team with Solec International (a PV module manufacturer) and the University of Massachusetts-Lowell/Center for Productivity Enhancement (automation specialists) who will act as lower-tier subcontractors. The effort is being addressed in two 1-year phases.

Springborn Laboratories *Photovoltaic Manufacturing Technology (PVMaT)* - Springborn will endeavor to solve problems related to the PV module encapsulant ethylene-vinyl-acetate (EVA) discoloration and/or degradation. Areas that will be addressed include a case history study and problem definition, identification of discoloration and/or degradation mechanisms, development of EVA-stabilization strategies, accelerated testing of new laminates, and pilot-scale production, and field-testing of new laminates. To conduct these efforts, Springborn is teaming with the Siemens Solar Industries; Photocomm, Inc.; United Solar Systems Corp.; Solarex Corp.; Texas Instruments; Solec International, Inc.; Utility Power Group, Inc.; Advanced Photovoltaic Systems, Inc.; Global Photovoltaic Specialists, Inc.; Arizona State University; Arizona Public Service Company; and the University of Connecticut. The effort is being addressed in three 1-year phases.
Objectives

The objectives of this program are to significantly advance the PV manufacturing technology, reduce module production costs, increase module performance and increase the production capacity of APS. The effort is divided into four separate tasks: new module designs, process and quality control, encapsulation improvements and automation of the manufacturing line.

Results

Four major achievements each representing one of the four tasks will be highlighted. They are the development of a higher power module, much improved uniformity for silicon deposition, an improved encapsulation process and the imminent completion of the new 12 MW APS manufacturing facility in Fairfield California.

Increased Power Module

While this program does not deal with deposition optimization other than through improved process and quality control, several changes to the module design were made under the program which resulted in a 10% increase in power output of our modules. This increase, together with the addition of a zinc oxide back coating capability in the Fairfield facility will allow APS to start production in that facility with a 60 W module.

Four separate contributions made this power increase possible. They were a 2.6% increase in active area, use of a higher haze tin-oxide, a thinner p-layer and most importantly a thinner i-layer. The larger active area was achieved by a more optimal module layout, and consisted of adding one cell and making all cells approximately 1% wider. The thinner i-layer was made possible by greatly improving the uniformity of silicon films as described below. The stabilized power increase resulting from the thinner i-layer is of the order of 5%, while the other three items add about 2% each. A fifth factor that will provide some additional gain will result from the better uniformity, since now all sections of the large module will have more uniform performance and hence internal mismatch losses will be reduced.
Uniformity improvements

Making uniform large area a-Si depositions presents several challenges, such as depositing uniform films over the entire 1.2 square meter area of the module. Uniform films are important for several reasons. First, appearance is important for some applications, e.g. architectural. Second, power losses result from mismatches within a module; this is more serious when additional layers such as would be needed for tandems structures are added. Third, in order to be able to laser scribe the thinnest parts of nonuniformly thick i-layers, the average silicon thickness has to be greater than what would be ideal from efficiency considerations.

The major causes of nonuniform deposition are chemistry, flow variations and rf. The fact that the deposition gases flow through the chamber and are partly consumed means that the gas composition changes. This change in gas composition results in a change in deposition rate of silicon and hence a variation in thickness over the area of a module. The rf problem exists because the dimensions of the glass are not negligible compared to the wavelength of rf used for the plasma; there is also a rf connection problem that leads to uneven deposition. Flow rates through the chamber are not totally uniform and hence different consumption rates and deposition rates apply at different positions on a module. Of these three factors, the variation in flows is the least important, while the other two are comparable.

Tools developed for quantifying the uniformity are an in-line thickness measuring device and a camera for capturing an image of each module. The thickness measurements are made at 25 points on each module and give quantitative information on the deposition uniformity, while the digital photograph provides input on a visual level. The photographic technique uses a digital camera to capture an image with a resolution of over 100,000 pixels per frame. By photographing the module through an interference filter at 580 nm, fringes separated by about 600 nm in thickness become very visible. The advantage of the photographic technique is that the entire module is analyzed rather than the coarse 5x5 grid of the other thickness measurement. Fig 1 is an image obtained with the digital camera and shows the uniformity typically obtained with a thin i-layer prior to any changes to improve uniformity. In this figure, every transition from dark to light to dark corresponds to approximately 600 nm.

To improve the uniformity, the three known contributors to nonuniformity were addressed. To deal with the chemistry and the rf effect, relative consumption rates were decreased by increasing flow rates and the rf feed point was changed so that the rf effect counteracted that due to gas composition changes. To reduce flow effects, the container in which the depositions are made was streamlined to have pressure drops where needed and minimized elsewhere. A photograph showing the uniformity attained with these changes is shown in Fig 2.
New Encapsulation Process

At the beginning of this year the time required to laminate a module was 10 minutes, too long to achieve the design capacity of 200,000 modules per year for the Fairfield facility. By doing the EVA curing in two steps, i.e. the split cure process, the time that the laminator is in use is cut in half. The first part of the cure is done in the laminator at lower than normal temperature and pressure. The second part is done in a separate oven. A side benefit of this procedure is that the second heating step is already required for curing the terminal cover and bracket adhesive. Therefore other than using a different temperature, no extra time is used up. Furthermore the thin film process employs a heat age step which can now be eliminated altogether since it is of the same duration and at the same temperature as the heating in the batch oven.

Thus several significant benefits result from adopting the split cure process. First a major piece of equipment, the heat age oven, is eliminated thereby reducing equipment costs, electricity usage and any yield losses that would normally be experienced in that equipment. The second benefit is that the very short laminator cure makes it possible to achieve the throughput rate that is needed; in fact that rate can be realized with only three laminators instead of the four that were acquired. A third significant benefit is that the cleaning that was required to remove excess EVA that was squeezed from between the two pieces of glass is essentially eliminated.

New Facility in Fairfield California

The benefits of the work performed under this contract to improve the APS manufacturing technology will come to fruition when the new 12 MW manufacturing facility begins operation.

An encapsulation line was installed earlier this year, and the thin film line is in the final stages of testing. It is expected that before the end of 93, modules will be made in the new facility and production will start in early 94. The thin film line is essentially fully automated with the exception of doors to the deposition system. Full automation of the encapsulation line is in the planning stages.
FIG. 1  Original Deposition Uniformity

FIG. 2  Deposition Uniformity with Process and Geometry Changes.
Title: Silicon-Film™ Photovoltaic Manufacturing Technology

Organization: AstroPower, Inc.
Newark, Delaware


Introduction

AstroPower is in the second phase of a three year project to upgrade its facility to produce 1.4 m² Silicon-Film™ photovoltaic modules with an output of 170 Wp. At present, efforts are focused on improving the production rate and material quality of the Silicon-Film fabrication machine; accelerating improvements in solar cell efficiency from 10% to 14%; and developing a large area module technology with efficiency improvements in parts handling. These efforts will significantly reduce material and labor costs. The capabilities for increased production capacity are being established by increasing machine production rates and automating solar cell processing to accommodate larger wafers. The key contract milestones are shown in Table I.

Approach

The Silicon-Film™ Process generates continuous polycrystalline silicon sheets that are fabricated into low-cost, large area silicon solar cells. The process is an inherently large area process with no fixed size limitations at this time. Because these sheets are produced at the desired thickness, ingot sawing and wafer polishing steps are eliminated resulting in a significant reduction in cost. The larger area and resulting higher power of the Silicon-Film products result in less handling and less labor per generated watt. The current project is focused on 15 cm wide sheets producing 15 cm by 15 cm solar cells.

Results

Wafer Machine Productivity and Efficiency Results

Key to developing the production process is the design and productivity of the wafer machine. The objective for Phase II was to demonstrate a continuous process capable of an overall production rate of 1.3 MW/year and a material use efficiency of 85%. We have met both of these goals. Production rate in megawatts per year is defined by the following equation:

\[ P_r = M_r \cdot N_0 \cdot Eff \cdot 10^{-5} \]

where \( P_r \) is production rate in megawatts per year, \( M_r \) is machine generation rate of usable wafer area in m² per hour, \( N_0 \) is the number of production hours per year, and \( Eff \) is the resultant solar cell efficiency. During Phase II, 10% efficient material was produced at a machine rate capable of 1.7 MW/year (assuming annual operation of the machine).
An important measure of wafer machine operation efficiency is the material usage efficiency. This is measured by taking the ratio of silicon in the finished wafer to the amount of silicon applied at the start of the wafer formation process sequence. Design, fabrication, and demonstration of continuous mode production during Phase II led us to a material use efficiency of 85% for formation of 15 cm by 15 cm wafers. This yield is the product of an applicator yield, a trimming yield and a visual/mechanical yield.

**Solar Cell and Module Results**

Silicon-Film™ solar cells were fabricated with 2.4 watts generated from 15 cm by 15 cm wafers. A current-voltage characteristic for one of these solar cells is shown in Figure 1. A large area (0.93 m²) module fabricated from 36 of these cells was measured at 78 watts. A current-voltage characteristic for this module is shown in Figure 2.

**Silicon-Film™ Technology Results**

The key determinant of solar cell device performance is the minority carrier diffusion length, L_n. Progress in material quality as the production process is developed is continually monitored by measuring L_n on quick-turnaround 0.2 cm² mesa solar cells. These cells are fabricated using the same basic junction formation and material processing steps as the large area production cells. Figure 3 shows the progress in improving diffusion length and its relationship to short circuit current as monitored by these small area devices (no anti-reflection coatings were used).

Following a concentrated effort on coupling crystal growth modeling with machine design, a Silicon-Film crystal growth regime was demonstrated that reached 50 micron diffusion lengths at sheet production rates capable of 1.7 MW/year. The key to this development was engineering and controlling the thermal environment of the Silicon-Film™ sheet during crystal growth. Device modeling shows that 50 micron diffusion length material will provide the foundation for the targeted 3.15 watt, AP-225 solar cell.

**Conclusions**

During 1993, five critical elements were achieved in the development of a Silicon-Film manufacturing technology. These elements are:

1. the construction and demonstration of a continuous-mode production machine,
2. the achievement of 50 micron diffusion lengths, using a modified crystal growth regime,
3. produced in a single machine at a rate of 1.7 MW/yr,
4. a 2.4 watt, 15 cm by 15 cm Silicon-Film™ solar cell,
5. a 78 watt, 36 cell module fabricated from 15 cm by 15 cm Silicon-Film™ solar cells.

The focus of our continuing efforts will be to develop these critical elements into AP-225, 3.15 watt solar cells; a 36 cell, 113 watt module; and a 56 cell, 170 watt module.
Table I. Silicon-Film™ Manufacturing Technology Milestones

<table>
<thead>
<tr>
<th></th>
<th>Phase I</th>
<th>Phase II</th>
<th>Phase III</th>
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</thead>
<tbody>
<tr>
<td>Wafer Machine</td>
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<tr>
<td>Production Rate</td>
<td>400 kW/yr</td>
<td>1.3 MW/yr</td>
<td>3.0 MW/yr</td>
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<tr>
<td>Material Use Efficiency</td>
<td>75%</td>
<td>85%</td>
<td>90%</td>
</tr>
<tr>
<td>Solar Cell Size*</td>
<td>a) 10 cm x 10 cm</td>
<td>b) 15 cm x 15 cm</td>
<td>b) 15 cm x 15 cm</td>
</tr>
<tr>
<td></td>
<td>b) 15 cm x 15 cm</td>
<td>c) 15 cm x 45 cm</td>
<td>c) 15 cm x 45 cm</td>
</tr>
<tr>
<td>Solar Cell Power</td>
<td>a) 1.1 watts</td>
<td>b) 2.5 watts</td>
<td>b) 3.1 watts</td>
</tr>
<tr>
<td>Module Power</td>
<td>--------------</td>
<td>84 watts</td>
<td>170 watts</td>
</tr>
</tbody>
</table>

* Product Identification: a) AP-100, b) AP-225, c) AP-675,

Figure 1. NREL Current-Voltage Characteristic of a 2.4 Watt AP-225 Silicon-Film™ Solar Cell

V\_\infty = 0.5757 \text{ V}  
I\_\text{sc} = 5.831 \text{ A}  
J\_\text{sc} = 24.63 \text{ mA cm}^{-2}  
Fill Factor = 72.46 \%  
V\_\text{max} = 0.4674 \text{ V}  
I\_\text{max} = 5.204 \text{ A}  
P\_\text{max} = 2432.2 \text{ mW}  
Efficiency = .10.3 \%
Figure 2. NREL Current-Voltage Characteristic of a 36 cell, 78 Watt Module Fabricated from AP-225 Silicon-Film™ Solar Cells

Figure 3. Data Showing Improvement in Diffusion Length that Led to Improvements in Short-Circuit Current (no anti-reflection coatings were used on these small area, 0.2 cm², test devices)
Objectives

The overall objective of this three year program is to advance ECD's roll-to-roll, triple junction photovoltaic manufacturing technologies, to reduce the module production costs, to increase the stabilized module performance, and to expand the commercial capacity utilizing ECD technology. The specific three year goal is to develop advanced large scale manufacturing technology incorporating ECD's earlier research advances with the capability of producing modules with stable 11% efficiency at a cost of approximately $1.00 per peak watt.

Approaches

We have performed manufacturing technology development work utilizing our advanced continuous roll-to-roll triple junction a-Si alloy solar cell production line, which was engineered and manufactured by ECD. The production line consists of: 1) a continuous roll-to-roll substrate washing machine; 2) a continuous roll-to-roll back-reflector machine; 3) a continuous roll-to-roll amorphous silicon alloy deposition machine; 4) a continuous roll-to-roll transparent conductor deposition machine.

The production line produces triple junction two band-gap a-Si alloy solar cells consisting of Si/Si/SiGe structure on a 5 mil. thick, 14 inches wide, 700 m stainless steel roll at a speed of 1 ft./min. This production line represents the world's first commercial production line which produces high-efficiency amorphous Si alloy solar cells utilizing multi-junction spectrum splitting cell design and high performance back-reflector.

Major Accomplishments

- We have successfully completed production runs in ECD's continuous roll-to-roll manufacturing line at production speed of 1ft²/min, which is required for the 2 Megawatt annual throughput.

- The cell efficiency that we have achieved for triple-junction spectrum splitting a-Si/a-Si/a-SiGe solar cell is 11.1%, which is the highest subcell efficiency of a-Si alloy solar cells produced in a high volume manufacturing line at full production speed. Figure 1 shows the J-V characteristic of an 11.1% solar cell. Figure 2 is the quantum efficiency curve (QE) of this solar cell. The short circuit current calculated from QE for AM1.5 Global spectrum for the top, middle and bottom component cells are 6.68 mA/cm², 7.26 mA/cm² and 7.34 mA/cm², respectively.

- 4ft² PV modules were assembled using a-Si alloy cells produced in a continuous roll-to-roll production machine. We have achieved initial aperture area efficiency of 9.5%, which is the highest efficiency for 4ft² a-Si alloy production modules. Figure 3 is the I-V curve of an ECD 4ft² triple-junction a-Si alloy PV module measured at NREL.
• The stable module efficiency of ECD's 4ft$^2$ a-Si alloy production PV module after 600 hours of light soaking under 1 sun at 50°C with load, is 8%. This is the highest stable module efficiency for a 4ft$^2$ a-Si alloy production module. Figure 4 is the I-V curve of an ECD 8% stable PV module, measured at ECD with a Spire 240A pulsed solar simulator. The I-V curve of the same module measured at NREL is shown in Figure 5. Figure 6 illustrates the semi-log curve of module efficiencies for two 4ft$^2$ modules as a function of light soaking time under 1 sun. The module efficiency has stabilized after 600 hours of degradation.

• We have made significant progress in ECD's PV technology during the last year, as indicated by the steady increase in the module efficiency. Table I lists the performance of all ECD modules delivered to NREL under PVMaT 2A program during the last year. All of ECD's progress and measurements are confirmed by NREL's measurement within its specified accuracy.

• We have achieved subcell yield of 99.7% for a 600m long production run. Figure 7 is a three-dimensional curve of subcell efficiency of 42 x 28 QA/QC subcells evenly collected along the 600m length and across the 14 in. width of the web. Only 3 out of the 1176 subcells are shunted.

• ECD has designed and constructed a multipurpose continuous roll-to-roll deposition machine for the manufacturing technology development. All of the Ag/ZnO back-reflector, triple-junction a-Si/a-Si/a-Si:Ge solar cell, and TCO layers can be deposited in the same continuous roll-to-roll machine.

References

Figure 1: J-V curve of a 0.25cm² triple-junction cell showing 11.1% efficiency.

Figure 2: Quantum efficiency curve for the 0.25cm² triple-junction cell showing 11.1% efficiency.

Figure 3: I-V curve of ECD's 4ft² triple-junction a-Si alloy PV module measured at NREL, showing 9.5% initial module efficiency.

Figure 4: I-V curve of 4ft² a-Si alloy PV module showing 8% stable module efficiency.
Figure 5: I-V curve of ECD's 4ft² a-Si PV module after 600 hours of light soaking, measured by NREL.

Figure 6: Module efficiencies of two 4ft² modules produced in ECD's manufacturing line, as a function of light soaking time.

Table 1: Efficiency data on 1ft. x 4ft. triple-junction modules.
Title: Photovoltaic Manufacturing Technology (PVMaT) Improvements for ENTECH's Concentrator Module

Organization: ENTECH, Inc., Dallas-Fort Worth Airport, Texas

Contributors: M.J. O'Neill, Program Manager
A.J. McDanal, Principal Investigator

Introduction

With significant assistance from the U.S. Department of Energy (DOE), Sandia National Laboratories (Sandia), and the National Renewable Energy Laboratory (NREL), the ENTECH technical team has been developing, field-testing, refining, and commercializing linear Fresnel lens photovoltaic concentrator technology for the past sixteen years. ENTECH's technology background, which includes four generations of the line-focus module, is summarized below.

Technology Background

<table>
<thead>
<tr>
<th>Time Period</th>
<th>Module Technology</th>
<th>Production Module Efficiency</th>
<th>Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>1978-82</td>
<td>First-Generation</td>
<td>11-13%</td>
<td>25 kW at DFW, TX</td>
</tr>
<tr>
<td></td>
<td>2.2 m², 25X, H₂O Cooling</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ASEC CZ SI Cells</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1981-84</td>
<td>Second-Generation</td>
<td>12-14%</td>
<td>22 kW at Sandia, NM</td>
</tr>
<tr>
<td></td>
<td>2.8 m², 40X, H₂O Cooling or Air Cooling</td>
<td></td>
<td>5 kW at TVA, TN</td>
</tr>
<tr>
<td></td>
<td>ASEC CZ SI Cells</td>
<td>(Lab Modules 17%)</td>
<td></td>
</tr>
<tr>
<td>1985-87</td>
<td>Third-Generation</td>
<td>13-15%</td>
<td>10 kW at Sandia, NM</td>
</tr>
<tr>
<td></td>
<td>2.8 m², 22X, Air Cooling Prismatic Covers</td>
<td></td>
<td>1 kW at PG&amp;E, CA</td>
</tr>
<tr>
<td></td>
<td>Solarex Pol Si Cells</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1988-92</td>
<td>Third-Generation</td>
<td>15-17%</td>
<td>300 kW at 3M, TX</td>
</tr>
<tr>
<td></td>
<td>2.8 m², 22X, Air Cooling Prismatic Covers</td>
<td></td>
<td>20 kW at PVUSA, CA</td>
</tr>
<tr>
<td></td>
<td>Solarex CZ Si Cells</td>
<td>(Lab Modules 21%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Prismatic Covers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1993-</td>
<td>Fourth-Generation</td>
<td>Higher Each Year</td>
<td>Utility-Scale &gt; 35 kW</td>
</tr>
<tr>
<td></td>
<td>3.1 m², 21X, H₂O Cooling or Air Cooling</td>
<td></td>
<td>(1 Tracker = 220 m²)</td>
</tr>
<tr>
<td></td>
<td>Cells from BP Solar, Deutsche Aerospace,</td>
<td></td>
<td>Remote &gt; 1 kW</td>
</tr>
<tr>
<td></td>
<td>Siemens &amp; Solarex Prismatic Covers</td>
<td></td>
<td>(SunLine Unit)</td>
</tr>
</tbody>
</table>

Objective

The key objective of ENTECH's PVMaT Program is to design, develop, and implement improved manufacturing processes for ENTECH's fourth-generation concentrator module. The improved processes are being engineered to simultaneously achieve enhanced product quality (i.e., improved module efficiency, reliability, and field lifetime), higher production volume (10 MW/year initial rate), and lower production costs ($1.25/W peak goal).
Approach

An outstanding international technical team has been assembled to improve the manufacturing processes associated with our fourth-generation linear Fresnel lens concentrator module. This team includes technical personnel from NREL (Rick Mitchell, Dave Mooney, John Benner, et al.), Sandia (Tom Hund, Alex Maish, et al.), 3M (Paul Jaster, DuWayne Radke, et al.), Consumers, Inc. (Arnie Kapitz), BP Solar (Tim Bruton and Jack Nagle), Deutsche Aerospace (Wilfried Schmidt), Siemens Solar (Kim Mitchell and Richard King), Solarex (John Wohlgemuth and Mohan Narayanan), Spire Corporation (Mike Nowlan), Texas Instruments (Hugh Wilson), Columbia Aluminum (Walt Brown), DuPont/Clear Solutions (Stan Levy), and key component suppliers, in addition to ENTECH's in-house staff.

Module Description

Our line-focus photovoltaic concentrator modules have been described in many previous publications. Fig. 1 shows a cross-sectional sketch of our fourth-generation module. The lens aperture is 85 cm (33.4 inches) wide by 366 cm (144 inches) long, for a total sun-capturing area of 3.1 m². Our production lenses provide a net optical efficiency of 90% while focussing sunlight onto 35 series-connected solar cells, each having active area dimensions of 4.1 cm (1.6 inches) wide by 9.65 cm (3.8 inches) long. Most of the focussed sunlight that would normally be lost between adjacent cells is recovered with simple "gap-eliminator" reflectors. The geometric concentration ratio of the module is 85 cm divided by 4.1 cm, which equals 21X. The module peak efficiency at standard test conditions (STC = 25C cell temperature and 1 kW/m² direct normal irradiance) is equal to the product of lens optical efficiency (90%), cell-to-receiver effective packing factor (95%), and cell efficiency. Three of our cell suppliers have already achieved about 18% peak efficiency in recent tests at Sandia. Thus, peak module efficiency is presently about 16%, corresponding to a power rating of about 500 W_peak. Clearly, our fourth-generation module is the largest photovoltaic module of any type yet produced, in terms of both aperture area and power output.

Significant Results During FY 1993

Concentrator Cell Improvements: Fig. 2 shows the basic layout of two of our concentrator cells on a standard 5-inch Czochralski silicon wafer. Fig. 3 shows our patented prism cover, which eliminates gridline obscuration losses for our concentrator cells. Our four cell suppliers have achieved excellent prism-covered cell performance results during FY 1993, as summarized below.

- **BP Solar** is developing a 39 cm², laser-grooved, buried contact cell for our concentrator module. The cell is being produced in Madrid, Spain. • Sandia-Measured Performance* (April 1993): 18.9% at 20 Suns, 25C.

- **Deutsche Aerospace** is developing a 39 cm², evaporated contact cell for our module. The cell is being produced in Heilbronn, Germany. • Sandia-Measured Performance* (April 1993): 18.9% at 20 Suns, 25C.

- **Siemens Solar** is developing a 39 cm², screen-printed contact cell for our module. The cell is being produced in Camarillo, California. • Sandia-Measured Performance* (April 1993): 17.0% at 19 Suns, 25C.

- **Solarex** is developing a 51 cm², mechanically grooved, buried contact cell for our module. The cell is being produced in Frederick, Maryland. • Sandia-Measured Performance* (April 1993): 18.9% at 20 Suns, 25C.
Cell Soldering Improvements: In the past, we have used stamped copper interconnects to extract the electrical current from the solar cell. Four stamped copper parts were joined to the four long edges of the solar cell (front and back) with a heat reflow soldering process, relying on solder paste, containing water-soluble flux. During FY 1993, we have adapted a proven one-sun cell soldering approach to our concentrator cell application. This approach employs mass-produced, solder-plated copper ribbon, which is joined to the solar cell via heat reflow after applying no-residue (no-clean) flux. Our team member, Spire Corporation, has developed an automated light-soldering process to implement the ribbon soldering approach.

Dielectric Improvements: Since the early 1980's, we have used alumina-loaded silicone rubber to bond the cell string to the heat sink. Unfortunately, this silicone material involved multiple labor-intensive, batch-process steps for mixing, stirring, applying, curing, testing, patching, and cleanup. During FY 1993, we have incorporated a mass-produced polymer film between the cells and heat sink. The selected film is DuPont Tefzel®, which provides excellent dielectric strength, high-temperature survivability, outstanding toughness, ease-of-use, and reasonable cost.

Heat Sink Improvements: In the past, our air-cooled receiver employed an extruded heat sink with a total fin area about twice as large as the lens aperture area. During FY 1993, our team member, Columbia Aluminum, has produced for us the world's largest extruded heat sink, which provides four times as much fin area as the lens aperture area. This new heat sink lowers the cell operating temperature by about 20 C, increasing module operational power output by 8-10%. Indeed, side-by-side outdoor tests have shown that the new heat sink allows the cell operating temperature for our concentrator module to be about the same as for a one-sun, flat-plate module.

Cost Impact: In previous fiscal years, we made major manufacturing advances for lenses, prism covers, module housings, etc. The combined impact of all of our PVMaT improvements on module manufacturing cost is substantial, even for relatively modest production rates, as summarized below.

<table>
<thead>
<tr>
<th>Cost Element</th>
<th>100 kW/year Production</th>
<th>3 MW/year Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Key Purchased Components (Costs Rounded to Nearest $0.10/W)</td>
<td>(Costs Rounded to Nearest $0.10/W)</td>
<td></td>
</tr>
<tr>
<td>Lens</td>
<td>$0.50/W</td>
<td>$0.30/W</td>
</tr>
<tr>
<td>Cells</td>
<td>$0.90/W</td>
<td>$0.40/W</td>
</tr>
<tr>
<td>Heat Sink</td>
<td>$0.30/W</td>
<td>$0.30/W</td>
</tr>
<tr>
<td>Housing (Box)</td>
<td>$0.60/W</td>
<td>$0.30/W</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>$0.20/W</td>
<td>$0.10/W</td>
</tr>
<tr>
<td>Total Cost of Key Components</td>
<td>$2.50/W</td>
<td>$1.40/W</td>
</tr>
<tr>
<td>Assembly of Cells, Receiver, &amp; Module</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cells &amp; Receiver</td>
<td>$0.60/W</td>
<td>$0.30/W</td>
</tr>
<tr>
<td>Module Assembly</td>
<td>$0.20/W</td>
<td>$0.10/W</td>
</tr>
<tr>
<td>Total Cost of Assembly</td>
<td>$0.80/W</td>
<td>$0.40/W</td>
</tr>
<tr>
<td>Total Direct Manufacturing Cost</td>
<td>$3.30/W</td>
<td>$1.80/W</td>
</tr>
</tbody>
</table>
Conclusions and Future Plans

Substantial progress has been made in developing the manufacturing technology needed to produce efficient, reliable, high-quality, low-cost concentrator modules. Unlike many other emerging photovoltaic technologies, our fourth-generation concentrator technology requires no further breakthroughs in materials, efficiency, stability, or basic manufacturing processes, to meet the Department of Energy's electrical energy cost goals. High-volume procurement of vendor-furnished parts, coupled with automated assembly of these parts into concentrator modules, will enable this technology to provide cost-effective electrical power in sunny regions of the world.

References

The Mobil Solar program in the DOE/NREL Photovoltaic Manufacturing Technology (PVMaT) Initiative is a three year program directed toward achieving cost reductions in manufacture of wafers of polycrystalline silicon. This is to be accomplished by improving yield and productivity in the growth of reduced thickness 200 micron octagons by the Edge-defined Film-fed Growth (EFG) technique, and in laser cutting of the octagons into 10 cm x 10 cm area wafers. The manufacturing advances made possible by technical achievements in the first 18 months of the Mobil Solar PVMaT program are shown to enhance future market share growth for its products as a consequence of significant reductions in a number of direct manufacturing cost elements in EFG wafer and module production.

Introduction

EFG octagon technology [1] allows growth of octagon-shaped hollow polycrystalline silicon tubes. The tubes are produced with lengths of 5 meters with area throughput rates of over 135 cm²/min per furnace. Octagons are cut by lasers into 10 cm x 10 cm polycrystalline wafers which are suitable for solar cell processing. This process avoids the customary slicing and grinding of ingots and polishing of wafers which are wasteful of material and are typical of most other wafer production methods.

The goals of the PVMaT program at Mobil Solar are to accelerate introduction of EFG technology advances in crystal growth and laser cutting needed for producing thinner wafers into the manufacturing line. The program is structured into three main tasks: to decrease the EFG octagon thickness; to increase the laser cutting throughput and improve wafer strength so as to enhance wafer yield of thinner material; and to improve crystal growth productivity. The technical accomplishments made in this program in the first 18 months are described in the next sections. This is followed by a presentation of the results of a cost model for EFG wafer and module production. This model gives an overview of the acceleration anticipated in the manufacturing cost reductions as a result of the implementation of the technical achievements of the PVMaT program.

Technical Achievements

The PVMaT program has two main areas of focus. In Phase I, we have accelerated the development and testing of EFG technology improvements vital to completion of the transition from growth of 400 to 300 micron thick octagons and cutting them into wafers, and incorporation of these advancements into the production line. At the same time, development work is in progress on high yield and productivity processes that will allow lowering of octagon thicknesses to 250 microns and cutting them into 10 cm x 10 cm wafers. Phase 2 work in progress continues to consolidate and optimize the growth and cutting of 250 micron thick material and is examining means by which to extend these gains further to 200 micron thicknesses. Details on the accomplishments in the three main tasks of the program described below are found elsewhere [2,3].

Thin Octagon Growth - Task I Specifications for two new EFG crystal growth furnaces have been completed and detailed engineering design work is in progress. One furnace is for growth of 300 micron thick octagons. The advanced features that will be incorporated into this furnace will result in increased furnace reliability, up time and throughput, and will increase 300 micron thick wafer quality. The other furnace design effort addresses a second-generation, advanced EFG growth system for thinner octagons. The projects to demonstrate approaches that improve octagon uniformity and properties, and enhance crystal growth productivity for the 250 micron thick octagons are on schedule and all of the Task I objectives for Phase I have been met [2]. Success in full scale implementation of
250 micron thick wafer processing is further dependent on achieving laser cutting improvements, described under Task 2 below, that will result from new wafer handling equipment and an improved wafer edge strength.

**Laser Cutting - Task 2** The Phase 1 objective in this task has focussed on evaluation of new laser configurations which can attain a higher quality cut, i.e., reduce the wafer edge damage. At the same time, we need to demonstrate that the new laser must have the potential for combining reduced damage cutting with an increase in cutting speed and laser cutting station wafering throughput.

Two types of lasers have been studied in detail in Phase 1: the dye laser, and the Nd:YAG laser. Feasibility studies on the dye laser demonstrated that it has the capability to achieve reduced damage cutting at the target throughput rates of this program. A cost analysis showed that at present it is too expensive to make the dye laser suitable for a production line environment. The scientific data obtained from the dye laser studies have been useful in identifying beam and cutting conditions for other cost-effective lasers for low damage and high throughput cutting of silicon. A new model of Nd:YAG laser has been feasibility tested in the laboratory and has been introduced for production line trials at Mobil Solar. This model has reduced cutting damage with only a small loss in throughput capability, and has a capital cost about a factor of two lower than the high throughput laser currently in use. This laser will be used in a configuration being tested for reduced-damage cutting at the Nd:YAG operating wavelength, which involves using a preheat beam. These tests are in the feasibility study stage.

New designs of wafer handling equipment for the cutting station have been completed and successfully tested at a prototype level. The equipment is currently under construction and will be introduced into the production line in the last quarter of Phase 2. This will lead to a factor of two increase in wafering rate of the laser station.

**Process Control and Product Specification - Task 3** Activities in this task are being carried out in support of the above two programs. Several new sensors are being evaluated for monitoring and controlling the EFG crystal growth process [2]. They are to be integrated in Phase 2 into control strategies based on Intelligent Processing of Materials (IPM) concepts to enhance yield and productivity in crystal growth. Wafer specifications are being developed for thickness uniformity, flatness, residual stress and wafer edge strength. A new effort has been organized in Phase 2 to address the generic issues related to electronic quality specifications for polycrystalline silicon. This work was described elsewhere [4].

**Cost Elements in EFG Wafer and Module Manufacture**

EFG technology advances developed in the PVMaT program are being integrated into the Mobil Solar production line on a continuing basis. Implementation of an improvement proceeds in several stages. These involve evaluations at all processing steps, from solar cell to module fabrication. The stages include: small batch processing, intermediate volume testing involving several thousands of wafers, and complete integration of the new technology on a side-by-side basis with the established line to demonstrate and evaluate the benefits of the improvements on a full cost basis.

Cost reductions that are anticipated from technology improvements generated in the PVMaT program are summarized in Fig. 1. The normalized cost plotted is the variable, or direct manufacturing cost, excluding capital cost and the cost of money. The individual contribution from a given advance in wafer production technology, which is the sole focus of the PVMaT effort, first is broken out separately. The module cost reduction is then calculated to reflect the contribution from this individual advance in wafer cost and is plotted additionally. Each new cost reduction is calculated using the previous improvement as the cost base, so that the final bars represent the cumulative cost reductions when all the advances are fully integrated into the manufacturing line.

Case 1 represents the cost baseline for 400 micron thick EFG wafers. The cases studied are as follows, with the time of introduction given in parentheses: Case 2 - wafer thickness reduction to 300 microns and average growth length per crucible extended by 28% (Phase 1); Case 3 - wafer flatness and cutting yield improvements, productivity increase in crystal growth (labor decrease)(Phase 2); Case 4 - new furnace and controls upgrading (Phase 2); Case 5 - laser cutting station throughput increase (Phase 2); Case 6 - wafer thickness reduction to 250 microns (Phase 3); Case 7 - advanced laser cutting station with throughput improvement of a factor of three over Case 5, and mechanical yield improvements (post-Phase 3); Case 8 - wafer thickness reduction to 200 microns (post-Phase 3); Case 9 - solar
cell efficiency increase from 13 to 15% (not part of PVMaT). Case 9 reflects the real impetus for achieving thinner wafers, which are needed to increase the yield of high efficiency cells. New schemes for solar cell design become accessible when wafer bulk diffusion lengths are consistently maintained of the order of the wafer thickness, and this will increase the percent of cells above a target level and make it possible to achieve the 15% efficiency levels with new designs.

Figure 2 illustrates the anticipated benefits of technology improvements casted in Fig. 1 on stimulating competitiveness of Mobil Solar products in photovoltaic markets. Here the technology cost benefits are related to Mobil Solar normalized historic module cost and production volume in a cumulative experience curve. Actual data are represented by rectangles and the top solid line and solid triangles represent the derived least squares fit cost projection. Considerable leverage in cost reduction is provided by the accelerated introduction of new PVMaT technology improvements developed under the PVMaT program, Cases 2-7. The vertical line terminating in the cross traces out the cumulative projected reductions of Cases 2-7 from Fig. 1., designated as Level 1 cost reductions. When these Level 1 cost reductions are fully integrated, the experience curve will shift downward to a new location, and a new trend line will be established for the experience curve. This is schematically indicated by the bottom dashed curve originating at the cross, drawn arbitrarily as the current 53% experience curve. Benefits of implementation of Level 2 (Cases 8 and 9) technology then further depress the trend line, as indicated by the second vertical line terminating as (+). The timing of the introductions will determine the exact magnitude of the cost benefits available from Cases 8 and 9, and these will not be necessarily as represented in Fig. 2.

Acknowledgements


References

Figure 1. Variable cost reduction elements for PVMaT program and beyond

Figure 2. Cumulative Experience Curve. The cost reductions projected for the PVMaT Program (X) and beyond (+) are also marked.
Introduction

Siemens Solar Industries (SSI) began a three-year, three-phase cost shared contract in March 1992 to demonstrate significant cost reductions and improvements in manufacturing technology. The work has focused on near-term projects for implementation in the SSI Czochralski (Cz) manufacturing facility in Camarillo, California. The work has been undertaken to increase the commercial viability and volume of photovoltaic manufacturing by evaluating the most significant cost categories and then lowering the cost of each item through experimentation, materials refinement, and better industrial engineering.

Objective

The objective of the program is to reduce costs in photovoltaic manufacturing by approximately 10% per year. The program consists of three focused tasks relating to cost reduction. The silicon wafer itself contributes about half of the total module cost and has the most potential for cost reduction. The cell processing costs are about a quarter of the module costs, with cell efficiency results being most important. Module assembly and packaging costs are the balance, with the module design, both materials and labor, contributing significantly. Overall, Environmental, Safety & Health issues govern the ability to commercialize processes and are significant items to address in increasing production volumes.

Approach

Task 1: Silicon Crystal Growth and Thin Wafer Technology. Crystal growing costs are driven by material growing yields and indirect manufacturing costs such as electricity and machine parts used each time an ingot is fabricated. Wafering costs are driven by labor and the number of good slices yielded per length of crystal processed. This first task of reducing the wafer costs has focused on the polysilicon material used for ingot growth, and the evaluation of wire saw machines to improve the yielded wafers per inch of ingot.

Task 2: Silicon Cell Processing. Cell processing costs are driven by the electrical contacts used, and the labor required for the process steps to clean the wafer, form the semiconductor junction, and the contacts. The cell tasks have been focused on better junction formation and reduced contact resistance. Implementation of lower labor cost, automated cell handling has started with robotic transfer mechanisms.
Task 3: Silicon Module Fabrication and Environmental, Safety, and Health Issues. Module costs are highly sensitive to labor and materials. The module design tasks are driven by high reliability in the field and lower costs. Included in this task is the environmental work to eliminate chlorofluorocarbon (CFC) usage and significantly reduce the caustic waste volumes.

Results and Discussion

During FY 1993 (10/01/92-9/30/93), several significant manufacturing technology improvements were achieved.

The Crystal Growing operation increased production significantly during the last year. The increase is attributable to several factors including improved poly quality and cleaning, upgrades to the growing equipment, specifically diameter controls, and upgrades to the hotzone parts which have increased reliability and reduced cycle time. A wide range of polysilicon starting materials have been evaluated. Crystal Growing yields, cell performance and impurity analysis have been conducted. Overall crystal growing yields improved by 8% as a result of the study.

A prototype, commercially available wiresaw was tested and a process developed for manufacturing silicon wafers for photovoltaic use. The development is ongoing with further process and equipment improvements anticipated. The average number of wafers per inch obtained to date on the wiresaw is over 40, which is a 38% yield improvement over the results obtained for ID sawn wafers. Two critical issues have been identified for additional yield improvement of the wiresaw process. These are the wire material itself, both strength and emper characteristics, and the slurry material, both the oil and the SiC grit. The material characteristics for the as received materials are the drivers here, and preferred suppliers are emerging.

Cell processing costs are driven by the amount of silicon used per cell (wafer thickness), the electrical performance of the cells, and the labor required for the processing of wafers into active cell devices. Work in this area has been focused on the reduction of labor through automation of various material transfer steps and the improvement of the electrical output of the cells processed by improving the contact resistance and diffusion processes. The cell electrical distribution has improved significantly as a result of improved contact and diffusion processes. Through experimentation with process changes a significant shift in the electrical distribution has been realized. This is shown in Figure 1.

Significant progress in cost reduction in module design has been made. Several items have been identified and implemented in manufacturing to reduce the final cost per watt of modules manufactured. The first of these improvements showed the use of anti-reflective glass etching to decrease the amount of reflected light on a module surface. Greater than a 1 Watt improvement in electrical power was seen on M55 (53 Watt) modules. A second item which showed significant benefit is the use of a "whiter" Tedlar™ backsheet which gave an overall 0.5 Watt gain in electrical performance on an M55 module. The use of "whiter" Tedlar™ has been implemented in full scale production. A third item in re-design of the junction box on the back of the module also contributed significantly to cost reduction.
Environmental, Safety and Health issues have also been addressed with the complete elimination of the use of CFC chemicals in the SSI manufacturing facility during the first half of 1993. This has been accomplished with the use of a no-clean solder flux paste.

**Summary**

Reduction in Cz photovoltaic manufacturing costs are driven by several parameters. Low wafer cost, high electrical and mechanical yields in fabricating cells, low labor in cell fabrication and module fabrication, and materials used for making modules are all significant factors. Siemens Solar has reduced costs by over 10% in one year by addressing each of these items. Table 2. shows the categories and total savings for manufacturing cost improvements effected this year. Further improvements in each area are planned.

Table 1. Cz manufacturing technology milestones.

<table>
<thead>
<tr>
<th>Task 1. Silicon Crystal Growth &amp; Thin Wafer Technology</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Increase Cz grower productivity by 25%</td>
<td>10%</td>
<td>15%</td>
<td>25%</td>
</tr>
<tr>
<td>B. Demonstrate utility of prototype wire saw</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Deliver 100 wire sawn wafers</td>
<td>*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C. Demonstrate 0.010-in-thick wire sawn wafers</td>
<td></td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>- Deliver 100 0.010-in-thick wafers</td>
<td></td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>D. Reduce wafer cost by 30%</td>
<td>15%</td>
<td></td>
<td>30%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Task 2. Silicon Cell Processing</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce cell cost by 30% ($/watt)</td>
<td>10%</td>
<td>20%</td>
<td>30%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Task 3. Silicon Module Fabrication &amp; Environmental, Safety &amp; Health Issues</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Reduce module fabrication costs by 35%</td>
<td>10%</td>
<td>25%</td>
<td>35%</td>
</tr>
<tr>
<td>- Deliver modules demonstrating reduced $/watt</td>
<td></td>
<td>2 modules (20%)</td>
<td>6 modules (25%)</td>
</tr>
<tr>
<td>B. Reduce caustic use and waste</td>
<td></td>
<td>25% reduction</td>
<td></td>
</tr>
<tr>
<td>C. Replace CFC's</td>
<td></td>
<td></td>
<td>90% reduction</td>
</tr>
<tr>
<td>Define process &amp; equipment</td>
<td></td>
<td></td>
<td>in CFC usage</td>
</tr>
<tr>
<td>Evaluate CFC alternatives</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Fig. 1. Electrical distribution improvement.

Table 2. Cost reduction summary.

<table>
<thead>
<tr>
<th>Category</th>
<th>% Reduction in Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 37 vs. 29 wafers/inch</td>
<td>6 %</td>
</tr>
<tr>
<td>2. 3% power increase due to cell improvements</td>
<td>2.5%</td>
</tr>
<tr>
<td>3. Module improvements</td>
<td>1.5%</td>
</tr>
<tr>
<td>- Whiter Tedlar</td>
<td></td>
</tr>
<tr>
<td>- Anti-Reflection glass</td>
<td></td>
</tr>
<tr>
<td>4. New J-box</td>
<td>1 %</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>11%</strong></td>
</tr>
</tbody>
</table>
INTRODUCTION
The goal of this project is to transfer the high efficiency multi-junction technology developed in R&D into the manufacturing environment. The principal challenges we face in this scale-up are maintaining uniformity over larger substrate area, developing processes that are robust and manufacturable, and containing/reducing costs in order to provide a competitive product.

In this paper we report the significant technical advances that have emerged from the jointly sponsored Solarex/NREL development under contract ZM-2-11040-2. Significant technical accomplishments include 1) Production of 0.1m² modules with initial efficiencies greater than 10.3% using manufacturing PECVD equipment 2) Initialization of large area PECVD, APCVD, vacuum sputtering, conductive frit application, laser scribing, and environmental testing equipment 3) Wet Hi-Pot encapsulation to greater than 2250 volts.

The structure of the contract is such that it is divided into 7 areas (tasks) of large area development: Front Contact, Laser Scribing, Amorphous Silicon Based Semiconductor Deposition Process, Rear Contact Deposition Process, Bus/Wire/Encapsulation/Frame, Material Handling, and Environmental Test/Yield/Performance Analysis.

DISCUSSION
The development of a large area APCVD system to deposit the front contact centered on the design and construction of a large area chemical injector. The chemical injector is used to introduce the reactants to the reaction chamber using a proprietary process. Since the process is atmospheric and thermally driven at the substrate surface, the uniformity of the resulting oxide film is largely a function of the uniformity of the reactant flows. The flow uniformity is determined by the ability to hold dimensional tolerance on the narrow injector slits used to introduce the chemical reactants. In principle, constructing such an injector is simple. There are, however, constraints on the system that make the design considerably more difficult. The reactants must be kept separate until each has reached the substrate surface -- otherwise the reaction will occur at the injector and obstruct the flow. The reactants are highly corrosive and the reaction chamber is in excess of 500 C greatly limiting the choice of materials used for the injector. The waste products must be carefully swept away to prevent particulate formation and maintain film uniformity. The entire assembly must be both durable and cost effective.
The laser scribing effort, Task 2, can be divided into three major areas. The first area of investigation has been development of new processes that result in better area utilization, reliability, and module efficiency. The different film layers were scribed using both IR and UV light. In addition, we optimized our techniques to improve the dimensional tolerance of our scribes in order to minimize the loss in active area. The second area involved an effort to develop a scribe, that when coupled with our encapsulant, provides a cost-effective way to protect the module against the corrosive effects of the environment while additionally preventing the flow of leakage current to the front of the module. Prior to the development of this new scribe, only 18% of the modules produced were able to withstand breakdown when tested wet at 2250 volts. Nearly 70% of the plates with the new scribe and identical encapsulant passed this test.

The third area of investigation was the development of large-area scribing capability. We now have the capability to scribe modules with areas exceeding 0.56 square meters. A real-time autofocus system, designed and tested on a smaller station, is being configured for use on the large area system. Scribe speeds have been increased to 0.23 m/sec.

Efforts in Task 3 were focused on transferring the R&D high efficiency multi-junction technology into a manufacturing and on initial operation of a large-area deposition system capable of depositing amorphous silicon on substrates up to 0.74 m$^2$ in size. An existing manufacturing load-lock system was used to deposit multi-junction devices on both 0.1 m$^2$ and 0.37 m$^2$ substrates. The highest power 0.1 m$^2$ device ever made at Solarex was produced in this manufacturing system. (Figure 1) The silicon system parameters have been optimized on these smaller size substrates to prevent the introduction of any confounding effects from the new, larger-area systems. Uniformity over the cathode area was exceptional: Three 0.1 m$^2$ substrates that were simultaneously deposited all had efficiencies over 9%. Transfer of this process to 0.37 m$^2$ has resulted in modules with power in the 25 watt range. The gap between these two efficiencies is narrowing as we optimize each of the large area processing steps.

The system that will be used to deposit multi-junction devices on substrates up to 0.74 m$^2$ has been initialized. The first silicon i-layer deposited in this system had uniformity better than 10% across the width and length of a 0.56 m$^2$ substrate. Several innovative designs have been incorporated in this system to improve both film uniformity and gas utilization. Film uniformity is needed to insure high multi-junction conversion efficiencies and high gas utilization is essential to insure low material costs. Multiple deposition chambers have been utilized to permit high speed processing of the multi-junction modules. Multi-zone heaters are used to minimize temperature non-uniformity throughout the chamber so that the film growth rates are uniform across the substrates.

Task 4 efforts were directed at providing a manufacturable method for depositing a high reflectivity back contact onto substrates up to 0.74 m$^2$ in size. A six-chamber metalization system was configured to DC magnetron sputter the back contact and to RF or DC magnetron sputter the high reflectivity ZnO. The current R&D method of depositing the ZnO is to RF sputter in multiple passes. We intend to investigate single-pass RF sputtering as well as reactive sputtering because of the potential to reduce manufacturing cost.
The uniformity of aluminum films deposited on 0.37 m$^2$ substrates was found to be within 10% of the nominal thickness across the substrate width. The oxide system has been fitted with a 450 kilohertz power supply and AC/DC combiner system to achieve the high deposition rates characteristic of DC sputtering and at the same time avoid the adverse effects of insulating layers that develop on the target surface during reactive sputtering. We continue to close the gap in conversion efficiency between devices coated in the research system and those deposited in the large-area system.

The work done under Task 5 fell into three broad categories. The first of these was the development of processes to deposit frit on a substrate up to 0.87 m$^2$ in area. Experiments were performed using a variety of application tips, substrate-tip working distances, material levels, and dispensing pressure to maintain the dimensional tolerance that is critical to insure maximum area utilization as well as proper adhesion of the soldered connector.

We also developed a connector that satisfies several important criteria: The connector must be weatherable, it must be able to withstand 2250 volts when wet, and it must be surface mountable. Screening of available candidates led us to enter a proprietary agreement with an established connector company to develop a suitable part.

The third area of focus was identify a coating that satisfied the requirements of ease of application, low cost, good weatherability, and high dielectric strength to withstand the 2250 volts of the wet hi-pot test. Experiments were performed to identify likely candidates by subjecting coated samples to environmental stress tests which included thermal cycle, UV exposure, illuminated water immersion, and cut tests for hardness. Failure analysis of modules that failed the hi-pot test indicated that pinholes in the encapsulant often acted as a conduit for the breakdown current. De-airing additives were added to minimize bubble formation during application and the coating thickness was increased.

Efforts under Task 6 were directed toward resolving the layout and material handling that will be required for a 10 Megawatt facility. To this end, consideration was given to effluent and utility requirements for this facility. Recently, we have begun to examine the costs that will be realized in the scale-up to 10 MW and how various components affect that cost.

Task 7 addressed the environmental testing of large area modules, the electrical cure and AM1.5 testing of large area modules, and the failure analysis and yield performance of our prototype line. The environmental test facility was adapted to accommodate larger modules in the interim test sequence (SERI/TR-213-3624) and we now have the capability to perform (or contract out) all the specified tests. The solar simulator was adapted and we routinely test large area modules. An electrical cure head had been obtained and a process developed to cure the electrical shorts in the thin film devices. Experiments to improve the yield were performed. One study revealed that depositing the back contact immediately following the silicon deposition, without allowing the plates to cool down, greatly reduced the number of modules having shorted segments. To understand the nature of yield losses, a database has been set up to record the critical process parameters as we begin to manufacture large-area multi-junction modules using our pilot line.
CONCLUSION
The ability to produce high efficiency triple-junction modules using manufacturing equipment has been demonstrated. An encapsulant and laser process has been identified that protects the module from high voltage discharge as well as from exposure to the environment. The scale-up of the equipment and processes needed to manufacture large area, high efficiency prototypes is nearly completed. This work has been jointly funded by NREL and Solarex under Subcontract Number ZM-2-11040-2

REFERENCES
1. United States Patents, #4,880,664 and #5,102,721.

![Figure 1: Current-Voltage characteristics of a module produced in a manufacturing system.](image-url)
Introduction

The objective of this research is to develop new processes for high throughput, high yield, fully automated interconnection of thin silicon solar cells. Improvements in ingot slicing (wire sawing) techniques are now enabling the production of Si wafers that are substantially thinner (~200 µm) than conventional wafers (350 to 500 µm). The use of these thin wafers can significantly reduce module manufacturing costs, provided that processing yields remain as high as they are now for standard thickness wafers.

We are currently developing an integrated system for interconnecting thin 200 µm cells. The system is designed to achieve high yield through low mechanical stress (handling) and low thermal stress (soldering) processes. The throughput goal is 15 cells per minute; at this rate, more than 5 MW of cells (with an area of 100 cm², efficiency of 12%, and 75% system uptime) can be processed annually in a 3 shift/day, 5 day/week operation.

Approach

An artist’s concept of the solar cell interconnecting system is shown in Figure 1. The system automatically produces multiple strings of interconnected solar cells from stacks of cells, reels of copper ribbon, and containers of liquid flux.

Interconnect ribbon is transported through a flux applicator that coats the ribbon with flux, a die that forms a stress-relief bend, and a knife set that cuts the ribbon to length. Two ribbons are processed side-by-side, resulting in a pair of cut, bent, and flux coated ribbons, or "tabs." Round or square cells up to 15 cm across can be processed. A vacuum chuck unloads a cell from a stack and places it face down on an aligner stage where a vision system inspects and locates the cell in x, y, and θ. A robotic manipulator arm aligns and places the cell on a pair of tabs, or if the cell fails inspection, in a reject stack. A vacuum conveyor belt holds the aligned tabs and cell and indexes them under a solder head which simultaneously solders front and back tabs to each cell. Series-connected cell strings are built up on the conveyor belt by repeating the tab fabrication and placement sequence, the cell inspection and alignment sequence, and the soldering process until the desired number of cells have been assembled together. Cell strings up to two meters long can be fabricated.

The completed string is positioned by the conveyor belt under a string transfer mechanism. The mechanism picks up the string and places it on an I-V tester that measures the string’s performance under simulated sunlight. If the string fails to meet selected criteria it is placed on
a reject carrier, while strings that pass are placed in sequence on a module carrier in the proper arrangement needed for assembling a complete module.

Current Status of Solar Cell Assembly Development

The mechanical design for the process subassemblies is now essentially completed. Subassembly testing, system integration, and software development are ongoing. A lay-out drawing of the integrated system is provided in Figure 2.

Solar cells are loaded from stack carriers rather than slotted cassettes to reduce the volume taken up by cells in process and also reduce the amount of operator handling. A two-stack shuttle system was designed that allows continuous cell feeding without interrupting the system for stack loading by the operator. A special vacuum pick-up was designed with a floating mount for handling thin cells with low mechanical force. The pick-up is mounted on a 2-axis (x, z) linear actuator that picks up the top cell in the stack and places it on the aligner stage.

The University of Massachusetts Lowell has the primary responsibility for the cell alignment process. A video camera, imaging board, and personal computer (PC) inspect the cell and determine its location in x, y, and θ. A 4-axis manipulator directed by the PC picks up the cell, transports it, and places it in the properly aligned position on the conveyor belt or on the reject elevator. An imaging board has been selected and various cameras and optics are being evaluated. The cell loading and alignment subassemblies have been fabricated and mounted on a common structural frame. Software development and testing are underway.

A number of processing subassemblies for ribbon feeding, fluxing, bending, cutting, and placing are designed, fabricated, and tested. The subassemblies are linked with various position sensors to a programmable logic controller (PLC) for automatic operation. Linear motors drive a ribbon shuttle assembly at high speed to cut and form tabs to user-specified dimensions. Ribbon flux coating tests are ongoing.

A specialized 3 m long vacuum conveyor belt assembly has been designed and fabricated. A heated platen supports the first 61 cm of belt. Perforations in the belt allow it to hold the tabs and cells in position with vacuum until they are soldered together. A solder head with high intensity lamps and an actuator have been fabricated and mounted over the belt. The belt is driven by a stepper motor programmed to set the spacing between cells and the number of cells in a string.

The heated conveyor section preheats the cells and tabs to reduce thermal shock and minimize heating time during soldering. The solder head’s high intensity lamps heat the cell with visible and infrared radiation, avoiding the thermal and mechanical shocks generated by conduction heating processes. Both the top and bottom tabs are soldered to the cell in a single operation, unlike conventional methods in which tabs are soldered to the cell’s top contact in one heating cycle and to the back contact in another.

The string transfer mechanism and string array table have been designed. The transfer mechanism has a linear array of vacuum pick-ups, one for each cell in the string, suspended on
a programmable 4-axis (x-y-z-θ) manipulator. The vacuum pick-up array can rotate 180° to place strings with their ends in alternating positive and negative directions to facilitate series connections between strings. An offset in the string length direction can also be programmed, a feature of particular use for round cells.

The string I-V tester design is underway. The tester comprises a solar simulator with a filtered pulsed xenon source for illuminating the string with an Air Mass 1.5 spectrum at an intensity of one sun (100 mW/cm²), an electronic load which sweeps the string’s current-voltage curve during a single lamp pulse, and a measurement system for processing the I-V data.

**Future Plans**

All subassemblies will be completed, tested and integrated to form a single automated processing system. System performance will be evaluated at Spire with several thousand thin (200 µm) cells to be supplied by Solec International. The system will then be shipped to Solec and evaluated in their module production line. Both at Spire and at Solec, system throughput and yield will be documented. Cells processed by the system will be monitored for performance (I-V curves) and the integrity of their soldered interconnects (pull tests, visual inspections).

**Publication**

A paper based on this work has been presented and submitted for publication.

Figure 1  Concept for an automated solar cell interconnecting system.

Figure 2  Drawing of the integrated cell assembly system (plan view).
Objectives

The objectives of this PVMaT R&D program are five-fold: 1) to better define the problem of yellowing/browning of EVA through literature search and field survey of case histories; 2) through comparative laboratory studies, determine probable mechanisms and the role of parameters such as heat, UV exposure, and module construction in the discoloration of EVA; 3) develop stabilization strategies for protecting EVA from degradation; 4) conduct accelerated laboratory and field testing of encapsulant-laminated test coupons and full modules in order to demonstrate the functional adequacy of the preferred stabilization strategies; and 5) implement these strategies by disseminating the information developed under this program and making the improved encapsulant sheet available to the PV industry.

Introduction

One component critical to the service life of PV modules is the useful life of the EVA encapsulant which is employed extensively by module manufacturers on a worldwide basis. This potent has been in commercial use since 1982, and over that time has proven to be a dependable material from the standpoint of production, module fabrication, and end-use. But despite the widespread acceptance of EVA for PV encapsulation, some module producers, end-users, and investigators have reported a yellowing or browning phenomenon with EVA in the field. While the incidence of this discoloration/degradation appeared isolated at the time that this present program was conceived, it raised serious concern as to the long term reliability of EVA encapsulated PV systems.

Prior to the start of this program, the discoloration of EVA, reported at the facility at Carrisa Plains, had been attributed to high operating temperatures, approximately 90°C, and increased light intensity resulting from mirror-enhanced light exposure. In addition, more than one of the manufacturers who supplied modules to the Southwest Regional Experimental Station (Southwest RES), in Las Cruces, NM, had reported browning of the EVA encapsulant at that site. One company reported cases of severe discoloration and loss of power, while another experienced only slight tinges of brown and yellow with essentially no power loss.

One PV module supplier to the Southwest RES reported signs of yellowing as early as 1984, only four years after installation of the array. By 1993, the condition
of these modules has deteriorated to a point where the cells are barely visible through the cover glass. Another supplier reported yellowing of EVA encapsulant in modules fielded in the Arizona desert, but at that time, similar installations located in Concord, MA (Northeast RES) and Cape Canaveral, FL (Southeast RES) had not exhibited discoloration of substantial degree.

However, despite the considerable discussion of yellowing/browning of EVA in the industry at the time this study was proposed to NREL, there was insufficient published information from which to draw meaningful conclusions regarding its causes. This fact prompted the following literature search and field survey to better define the problem.

Technical Approach

Using a computerized literature search, phone survey, field visits, and a written questionnaire, detailed information was gathered regarding module design and construction, fabrication/curing techniques, use of primer, grade and supplier of EVA sheet, type of modules, field exposure conditions - especially operating temperature and solar insolation, etc. The primary purpose of this initial literature search/survey investigation was to establish correlations between these variables and the incidence of EVA discoloration, leading to a more detailed investigation of causes and mechanisms later in the program.

Results

A thorough review of the literature on thermal and photothermal degradation of EVA, plus a survey of case histories of discoloration of EVA-based encapsulants in fielded flat-plate PV modules has solidified some significant findings regarding EVA yellowing/browning.

The literature reveals that EVA will undergo thermolysis of the acetate groups at temperatures of 130 to 150°C and above, leading to the formation of double bonds in the backbone of the copolymer. EVA copolymers, especially those such as Elvax 150 with comparatively high vinyl acetate contents, tend to contain blocks of vinyl acetate homopolymer. These blocks, when exposed to elevated temperatures, will yield conjugated unsaturation or "polyenes" that result in a yellow to brown color in the material.

This phenomenon has also been evident with combined U.V. radiation and heat, but at moderate conditions (i.e. U.V. radiation of one sun or temperature of less than 125°C), temperature or U.V. alone appear insufficient to cause the discoloration. At moderate conditions, both U.V. and heat are required.

Also, in laboratory studies the EVA discoloration has been found to be accelerated by metal (e.g. silver and copper) and metal oxide interfaces such as those found in cell grid lines.

It is also evident, that the formation of polyenes in the EVA is but an intermediate step in the overall photooxidative degradation process which leads to chain scissioning and crosslinking and loss of ultimate tensile elongation,
but does not seem to affect the elasticity of the EVA at low elongations. Further oxidation or photooxidation of the polyenes can also lead to apparent "bleaching" of the yellow-brown color.

The survey of case histories of EVA-based encapsulant discoloration in fielded modules in the U.S. (see Table 1) reveals that the problem is limited to those areas of the West and Southwest that have comparatively high solar insolation and ambient temperature. We have seen no reported cases of discolored EVA-based encapsulant from modules fielded in the Northeast, Central U.S., or Western Europe.

The absence of hard data regarding module operating temperatures, solar insolation, the onset of discoloration, and quantitative information regarding the degree of discoloration has made any correlations between various fabrication, placement, and operating conditions and the incidence of discoloration difficult if not impossible. However, the degree of discoloration does appear to loosely correlate with increasing average daily direct normal solar radiation and approximate maximum module operating temperature, as estimated from maximum ambient temperatures (see Figure 1).

In addition, it is clear that the discoloration problem is not limited to the modules of any one manufacturer. Discoloration in the EVA encapsulant has been experienced in fielded modules from all major U.S. module producers. However, the rate and degree of discoloration do appear to vary from company to company.

Finally, discoloration is not limited to the EVA encapsulant sheet from any one supplier.

---

**Figure 1**

The Effects of Radiation and Module Temperature on EVA

<table>
<thead>
<tr>
<th>Location</th>
<th>Ave. Annual Radiation kJ/m²</th>
<th>Approximate Av. Annual Module T(°C)</th>
<th>Degree of Browning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phoenix</td>
<td>21216</td>
<td>60</td>
<td>moderate</td>
</tr>
<tr>
<td>Austin</td>
<td>16755</td>
<td>56</td>
<td>slight</td>
</tr>
<tr>
<td>Las Cruces</td>
<td>21559</td>
<td>55</td>
<td>slight</td>
</tr>
<tr>
<td>Sacramento</td>
<td>18645</td>
<td>53</td>
<td>slight</td>
</tr>
<tr>
<td>Albuquerque</td>
<td>20740</td>
<td>51</td>
<td>slight</td>
</tr>
<tr>
<td>Boston</td>
<td>12537</td>
<td>45</td>
<td>no browning</td>
</tr>
<tr>
<td>Denver</td>
<td>17800</td>
<td>38</td>
<td>no browning</td>
</tr>
</tbody>
</table>
Table 1 - The History of Fielded, EVA-Encapsulated PV Modules

<table>
<thead>
<tr>
<th>Location</th>
<th>Mfg</th>
<th>EVA Source</th>
<th>Formulation</th>
<th>Color</th>
<th>Approx. Max. Temp.</th>
<th>Observation Time</th>
<th>Construction (b)</th>
<th>Elevation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWRES Las Cruces, NM</td>
<td>A</td>
<td>-</td>
<td>A9918</td>
<td>brown</td>
<td>-</td>
<td>3-4 years</td>
<td>-</td>
<td>1198 m</td>
</tr>
<tr>
<td>Hawaii</td>
<td>B</td>
<td>a</td>
<td>A9918P</td>
<td>clear</td>
<td>-</td>
<td>4 years</td>
<td>B</td>
<td>-</td>
</tr>
<tr>
<td>Detroit</td>
<td>B</td>
<td>a</td>
<td>A9918P</td>
<td>clear</td>
<td>-</td>
<td>4 years</td>
<td>B</td>
<td>191 m</td>
</tr>
<tr>
<td>California</td>
<td>B</td>
<td>a</td>
<td>A9918P</td>
<td>clear</td>
<td>-</td>
<td>4 years</td>
<td>B</td>
<td>-</td>
</tr>
<tr>
<td>San Ramon, CA</td>
<td>C</td>
<td>b</td>
<td>other</td>
<td>brown</td>
<td>64°C (c)</td>
<td>4-5 years</td>
<td>B</td>
<td>8 m</td>
</tr>
<tr>
<td>Davis, CA</td>
<td>D</td>
<td>c</td>
<td>A9918</td>
<td>brown(d)</td>
<td>-</td>
<td>4-5 years</td>
<td>D</td>
<td>8 m</td>
</tr>
<tr>
<td>China Lake, CA</td>
<td>A</td>
<td>-</td>
<td>A9918P</td>
<td>clear</td>
<td>-</td>
<td>5 years</td>
<td>A?</td>
<td>-</td>
</tr>
<tr>
<td>China Lake, CA</td>
<td>E</td>
<td>a</td>
<td>A9918</td>
<td>brown</td>
<td>-</td>
<td>5 years</td>
<td>-</td>
<td>681 m</td>
</tr>
<tr>
<td>Sells, AZ</td>
<td>C</td>
<td>b</td>
<td>other</td>
<td>80% brown</td>
<td>-</td>
<td>6-8 years</td>
<td>B</td>
<td>-</td>
</tr>
<tr>
<td>City of Austin, TX</td>
<td>D</td>
<td>c</td>
<td>other</td>
<td>slight brown</td>
<td>60-71°C (3),(e)</td>
<td>7 years</td>
<td>B</td>
<td>250 m</td>
</tr>
<tr>
<td>SMUD, CA</td>
<td>D</td>
<td>c</td>
<td>A9918</td>
<td>light amber</td>
<td>65°C (f)</td>
<td>7 years</td>
<td>B</td>
<td>8 m</td>
</tr>
<tr>
<td>Caples Lake, CA</td>
<td>C</td>
<td>b</td>
<td>other</td>
<td>clear</td>
<td>52°C (g)</td>
<td>&gt; 7 years</td>
<td>B</td>
<td>2400 m</td>
</tr>
<tr>
<td>Carreira Plains, CA</td>
<td>C</td>
<td>b</td>
<td>other</td>
<td>slight brown</td>
<td>-</td>
<td>8 years</td>
<td>B,D</td>
<td>640 m</td>
</tr>
<tr>
<td>John Long, Phoenix, AZ</td>
<td>C</td>
<td>b</td>
<td>other</td>
<td>moderate</td>
<td>77°C (3)</td>
<td>8 years</td>
<td>B</td>
<td>340 m</td>
</tr>
<tr>
<td>Sandia, Albuquerque, NM</td>
<td>D</td>
<td>d</td>
<td>A9918</td>
<td>light amber</td>
<td>-</td>
<td>8 years</td>
<td>B</td>
<td>1619 m</td>
</tr>
<tr>
<td>SMUD, CA</td>
<td>C</td>
<td>b</td>
<td>other</td>
<td>slight brown</td>
<td>77°C (3)</td>
<td>9 years</td>
<td>B</td>
<td>10 m</td>
</tr>
<tr>
<td>San Ramon, CA</td>
<td>F</td>
<td>c</td>
<td>A9918P</td>
<td>clear</td>
<td>-</td>
<td>9-10 years</td>
<td>B</td>
<td>8 m</td>
</tr>
<tr>
<td>Carreira Plains, CA (h)</td>
<td>C</td>
<td>b</td>
<td>other</td>
<td>dark brown</td>
<td>80-90°C (b)</td>
<td>10 years</td>
<td>B,D</td>
<td>640 m</td>
</tr>
<tr>
<td>Costa Rica</td>
<td>G</td>
<td>-</td>
<td>A9918</td>
<td>clear</td>
<td>-</td>
<td>10 years</td>
<td>B,C</td>
<td>-</td>
</tr>
<tr>
<td>Mohave Desert</td>
<td>E</td>
<td>a</td>
<td>A9918</td>
<td>clear</td>
<td>-</td>
<td>10 years</td>
<td>B</td>
<td>-</td>
</tr>
<tr>
<td>&quot;Around the World&quot;</td>
<td>E</td>
<td>a</td>
<td>A9918</td>
<td>clear</td>
<td>-</td>
<td>10 years</td>
<td>B</td>
<td>-</td>
</tr>
<tr>
<td>Cape Canaveral, FL</td>
<td>A</td>
<td>-</td>
<td>A9918</td>
<td>discolored</td>
<td>-</td>
<td>10 years</td>
<td>A</td>
<td>-</td>
</tr>
<tr>
<td>SWRES Las Cruces, NM</td>
<td>D</td>
<td>c</td>
<td>A9918</td>
<td>light amber</td>
<td>75°C (6)</td>
<td>10 years</td>
<td>B</td>
<td>1198 m</td>
</tr>
</tbody>
</table>

(a) Estimated, no "hard" data available, (summer) measurements taken mostly from back-side of module
(b) A- Glass/EVA/Cell/EVA/Foil, B- Glass/EVA/Cell/EVA/Film laminate, C- Tefzel/EVA/Cell/EVA/Film laminate, D- Bifacial
(c) Average ambient temperature plus 30°C
(d) Browning varied from one cell to another within the same module
(e) High and low mounted racks
(f) Manufacturer's data
(g) Estimated based on high wind velocity (ambient temperature plus 20°C)
(h) Modules operated at approximately 2 suns (mirror enhanced)
Objective

The objective of this project is to significantly advance the photovoltaic manufacturing technologies, reduce module production costs, increase average module performance, and increase the production capacity existing in Utility Power Group (UPG) and Advanced Photovoltaic Systems (APS). Areas of focus include:

- Encapsulation and Termination
- Product Design
- Process and Quality Control
- Automation

Utility Power Group has improved upon the previous UPG encapsulation system through the development of advanced encapsulation materials and processes which have resulted in a module that does not require backing glass. In addition, UPG has developed advanced termination materials and processes.

UPG POWERGLASS Module Encapsulation

Utility Power Group has developed an advanced encapsulation system for its manufacturing line. Particular emphasis has been given to the simplification of the conventional glass/EVA/glass module structure, wherein the superstrate glass is tempered and coated with a high performance encapsulant, thereby eliminating the need for a back glass sheet. UPG has investigated a wide range of materials for single and multi-layer encapsulation systems, as well as selected vendors to demonstrate the feasibility of superstrate glass tempering. All materials have been evaluated in terms of the level of environmental protection provided to the thin-film module, manufacturing cost reduction and PV systems related factors. Prototype modules have been
produced for evaluation by potential and existing customers, and when required, design modifications have been performed. Prototype modules have been subjected to accelerated life testing. The goal of this task was to obtain a cost reduction of 35% in the UPG encapsulation process. UPG has significantly improved upon that goal by demonstrating an encapsulation system which is 65% lower in cost than the previous glass/EVA/glass system.

UPG POWERGLASS Module Termination

Utility Power Group has optimized the materials and processes utilized in the electrical termination of the POWERGLASS module. The technical approach has been to design and fabricate several candidate POWERGLASS module termination configurations to be compatible with the candidate encapsulation materials and processes. All termination components were designed for use with automated insertion and assembly equipment (robotic "pick and place"). All designs were analyzed in terms of manufacturing cost reduction of the former process and ease of use from the customers' viewpoint. Upon completion of design and fabrication, candidate terminals were attached to POWERGLASS modules for evaluation and testing. The goal of this task was to yield an optimized terminal material, process, and configuration for the POWERGLASS module capable of demonstrating a cost reduction of 50% from the former termination system. UPG has improved upon this goal through the realization of a 65% reduction in termination cost.
Figure 1: Manufacturing cost reduction of the termination and encapsulation process steps as a result of the PVMaT effort. The Pre-PVMaT bar represents the combined costs of termination and encapsulation prior to the start of the PVMaT project. The PH1-Goal bar represents the original PVMaT first year goal set for termination and encapsulation cost reduction. The PH1-Result bar represents the actual result of the PVMaT first year effort.

Figure 2: Cost reduction projections of the termination and encapsulation process steps as a result of the three-year effort under the PVMaT project. Due to the success in cost reduction during the first year, UPG has set new cost reduction goals for the second and third years.
Figure 3: Ratio of the costs of the termination and encapsulation process steps to the balance of the process steps for the Pre-PVMaT modules.

Figure 4: Ratio of the costs of the termination and encapsulation process steps to the balance of the process steps for the Post-PVMaT modules.
Objectives

The Photovoltaic Module and System Performance and Engineering-Project is an integral element of the NREL Photovoltaic Program. A primary goal of the engineering project is to ensure that state-of-the-art PV capabilities are available as resources for cooperative research and utilization by the U.S. PV community. Those capabilities include equipment, facilities, and related technical expertise, e.g., participating in PV standards and codes development, and providing support to industry, utility, and others interested PV technology. The engineering project is responsible for conducting PV module, system, and solar radiometric research, engineering, testing, evaluation, and analysis. Technical results and solutions to issues are provided including developing criteria for test and evaluation procedures, and verifying PV performance. The engineering project complements all the other NREL PV Program projects in addition to assisting National Photovoltaic Program activities conducted or managed through DOE headquarters, the DOE Golden Field Office, and Sandia National Laboratories.

Technical Approach

The project primarily includes NREL in-house activities and a small number of subcontracts. The project is organized under the primary areas shown in Figure 1.

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**Figure 1. PV Module and System Performance and Engineering Project Contacts**
PV Efficiency Measurements — Standard Reporting Conditions. The performance of PV devices of all sizes and technologies are evaluated by providing secondary calibrations of PV cells, efficiency measurements with respect to standard reporting conditions, efficiency verification of subcontract deliverables, and current-voltage (I-V) measurements under varying temperature, spectral irradiance, and total irradiance. Capabilities also support the entire PV community by providing information on PV measurement equipment and systems appropriate for the end user, I-V measurement procedures, and measurement uncertainty analysis; and being committed to obtaining the lowest possible uncertainty in the measurement of the standardized PV performance of single- and multi-junction cell and modules. Included in the uncertainty analysis are the determination of potential artifacts in the I-V results because of equipment or procedures, and realistic estimates of the elemental error sources. Spectral irradiance measurements and modeling, and PV performance modeling is also provided in support of ongoing cooperative research efforts with other groups.

PV Module Materials and Encapsulation Research has focused on polymeric pottant materials, building on past successes such as identifying the causes of failure or change in ethylene vinyl acetate (EVA) that limit the service life or reduce the performance of PV modules. Ongoing focus is directed at developing new or improved pottant materials, documenting degradation and failure mechanisms that can be used to guide research to identify improved materials, and understanding PV-specific compatibility and durability intrinsic problems at material interfaces in cells/modules. The technical approach consists of conducting experimental work, interpreting the results, establishing test methods, and seeking solutions in concert with industry.

PV Module Qualification Testing and Test Method Development assists in identifying failure modes, developing new qualification tests, and acquiring and analyzing field failure data, all leading to better module designs. Activities determine the effects of qualification tests and the sensitivity of each test that is conducted. Correlation of accelerated testing and real-time exposure is being evaluated, and failure mechanisms are being identified with recommended solutions. New accelerated test methods are being explored to reproduce failures observed in the laboratory and reported from the field.

PV Module and System Technology Validation encompasses activities for designing, constructing, and monitoring the performance of emerging PV modules and small systems (e.g., 1 kWp each) at the NREL PV field site or at user locations. Capabilities include module/array stability testing, light soaking, and thermal annealing of thin-film modules under outdoor and simulated environmental test conditions; in summary:

- Module testing at STC and under prevailing (outdoor) conditions
- Module qualification testing
- Array testing
- System design
- System modeling
- System analysis
- System instrumentation
- System monitoring
- Array support structures capable of hosting five 1-kW PV systems in a utility-interactive mode
System performance activities also included supporting the Photovoltaic for Utility Scale Applications (PVUSA) Project, Niagara Mohawk Power Company, and the U.S.-Brazil electrification projects (e.g., Technical Review Committee member and providing additional technical support), and managing the "Amorphous Silicon Utility/Industry PV Power Project" that includes a-Si module development, module qualification testing, and ultimate deployment and monitoring of systems in the field at different locations throughout the country.

**PV Solar Radiation Research** directly supports characterizing, measuring, testing, designing, and understanding the performance of PV cells, submodules, modules, and systems by providing a scientific and engineering understanding of incident solar irradiance, and through developing instruments and/or measurement methods. The approach focuses on providing integrated technical support, e.g., developing and providing broadband and spectral radiometric measurements; and instrument calibrations, characterization, and utilization to assist PV performance measurements. The approach includes operation of reference radiometric sensors, calibration of solar simulators, and development and operation of a reference irradiance and meteorological station at NREL.

**PV Test Method Validation and Testing Certification Criteria.** The focus is on assisting in coordinating the consensus development of PV standards, codes, and criteria for test and evaluation procedures. The approach includes participating and performing major leadership roles in the IEEE Standards Coordinating Committee 21 and in the ASTM Subcommittee E44.09, conducting round-robin cell and module test method verification, developing criteria for module certification and test facility accreditation through the PV community with balanced industry representation and subcontract support, revising the National Electric Code PV Articles, developing PV energy rating standards, and working in the international arena, e.g., through the NREL-managed Solar Energy Industry Association (SEIA) subcontract for International Electrotechnic Committee TC-82 secretariat and U.S. Technical Advisory Group coordination of international PV standards development.
Title: PV Efficiency Measurements - Standard Reporting Conditions

Organization: NREL PV Module and Systems Performance and Engineering Project

Contributors: K.A. Emery Team Leader; S. Rummel, Y. Caiyem, H. Field, D. Dunlavy

Objectives
The performance of photovoltaic devices of all sizes and technologies are evaluated by this activity. This team supports the entire photovoltaic community by providing: secondary calibrations of photovoltaic cells, efficiency measurements with respect to a given set of standard reporting conditions, efficiency verification of contract deliverables, current versus voltage (I-V) measurements under varying temperature, spectral irradiance and total irradiance. This activity also supports the entire PV community by providing information on: PV measurement equipment and systems that are appropriate for the end user, I-V measurement procedures, and uncertainty analysis. Included in the uncertainty analysis are the determination of potential artifacts in the I-V results because of equipment or procedures, and realistic estimates of the elemental error sources. This activity is committed to obtaining the lowest possible uncertainty in the measurement of the standardized PV performance of single- and multi-junction cell and modules.

Technical Approach
The photovoltaic current versus voltage characteristics are measured with respect to standard terrestrial reporting conditions (25°C temperature, 1000 Wm⁻² total irradiance and ASTM E892 global reference spectrum). The intensity of the Spectrolab X-25 solar simulator is adjusted until the measured short-circuit current of a reference cell is equal to its calibration value corrected for spectral mismatch. The current versus voltage characteristics are then measured using 4-terminal Kelvin connections to the PV device with a custom data acquisition system designed to give a random error of less than ±0.1% and a non random error of less than ±1%. The I-V system has a voltage range of ±50V (0.1 µV resolution) and ±8A to ±1 pA. These procedures have been shown to be valid for any given tabular reference spectrum including AM0 and the ASTM direct normal reference spectrum. Because of the wide current and voltage range the system is also used for concentrator and dark I-V measurements. For two-terminal multi-junction devices the spectrum of the Spectrolab model X25 solar simulator is adjusted, using a special filter plate developed at NREL, until each junction is producing the correct photo-current. In the limit as the number of junctions becomes 1 the multi-junction and single-junction measurement procedures are identical. The I-V system is also used for examining the effects of maximum power versus illumination time, Voc vs. time, and Isc vs. time on the PV performance. This system is also used to examine hysteresis related artifacts.

The spectral response measurement system uses periodic (440 Hz) monochromatic light directed through one of 51 10 nm bandwidth interference filters covering the spectral range from 290 to 2000 nm. The system is capable of providing steady-state light bias levels up to 2A and voltage bias levels from ±1 mV to ±40V. The intensity of the bias light is normally adjusted to give the short-circuit current under standard reporting conditions. The custom operational amplifier based data acquisition system allows for a wide range of gains (1 to 10⁶) allowing for a wide range of areas (less than 0.01 cm² to over 1000 cm²) with a wavelength dependent error of less than ±5% and a error of less than ±2% in the integrated absolute quantum efficiency.
The efficiency versus concentration measurements are measured with an unfiltered 1000W Xe-arc light source that is focused to a small area, and the one-sun data acquisition system described above. Using the cell $I_{sc}$ measured at one sun (ASTM E891-87 direct normal reference spectrum at a total 1-sun irradiance of 1000 Wm$^{-2}$) and assuming linearity in the current with total irradiance, the I-V characteristics are measured. Using a technique developed at NREL the temperature of the space charge region temperature can be accurately set to a given value even though large temperature gradients (>10°C) may exist between the plate temperature and junction temperature. The procedure involves setting the sample temperature to the reference temperature e.g. 25°C without illumination (no heat load). Using a high speed shutter and voltmeter the open-circuit voltage is sampled (1000 readings / sec). The highest measured $V_{oc}$ is then taken to be the $V_{oc}$ under concentration. The thermoelectrically controlled vacuum plate is then cooled until this $V_{oc}$ is reached.

The short-circuit current, total irradiance, and spectral irradiance are measured at the same time outdoors with the same field of view. The total irradiance is measured with a primary absolute cavity radiometer with a 5.00° field of view, and the spectral irradiance is measured with a LICOR LI-1800 spectroradiometer with a 5.00° field of view. The uncorrected average calibration value $<CV_u>$ is calculated for the 30 Isc and Etot readings taken during the 30 seconds required to measure $E_s(l)$. The atmospheric constraint for a valid calibration value is that the range (maximum to minimum) over the 30 second time period in Isc be less than 0.25%, in Etot be less than 0.07%, and in $<CV_u>$ be less than 0.1%. Once a valid $<CV_u>$ is obtained the short-circuit current is corrected for temperature to 25°C and the spectrally corrected calibration value $CV$ is computed. Since the measurement of $E_s(l)$ does not encompass the limits of the reference spectrum, the measured spectrum is extended using a computer model to encompass the range of the reference spectrum (300-4000 nm). The calibration value $CV$ is computed at least 20 times for at least 3 separate days giving a single calibration value. This procedure has been shown to have a total uncertainty of less than ±1%.

The I-V characteristics of modules are routinely evaluated using the Spire 240A solar Simulator. This system has a 0-100V and 0-20A range for a 61 by 122 cm area. Because the Spire 240A simulator consistently underestimated the fill factor for high capacitance modules, Spire Corp. modified their data acquisition hardware and software ("peak detector") to correct this problem in early 1992. During FY 93 NREL evaluated four different versions of the peak detector board supplied by SPIRE before settling on the version currently in use. The Spectrolab Large Area Pulsed Solar Simulator (LAPSS) produces a one-sun beam of light (2m by 2m area and could illuminate a 4m by 4m area). The custom I-V system of the LAPSS has 3 modes of operation: capacitive sweep from Isc towards $V_{oc}$, current at a fixed power supply voltage, and bi-directional sweeping over a user defined or automatically determined voltage range. The system is designed to handle ±200V maximum (1 µV minimum), ±30A maximum (0.01 mA minimum) with 10 voltage and current ranges to ensure accuracy. The concentrator lamp housing allows measurement to 2000 suns.

During FY93 standardized Outdoor module I-V measurements were performed on a variety of one-sun and concentrator modules using one of two fixed-tilt platforms or a 2-axis Martin Marietta Tracker. For flat-plate modules the total irradiance was measured with an Eppley pyranometer and a crystal-Si reference cell in a module package mounted in the plane-of-array.
A normal incidence pyrheliometer calibrated against NREL's cavity radiometers is used to measure the direct normal irradiance for concentrator modules. The module temperature is measured with a platinum RTD temperature sensor attached to the back surface of the module. The spectral irradiance is measured during the I-V measurement using a LICOR LI-1800 spectroradiometer with a Teflon dome and temperature controlled detector. Meteorological parameters at the time of measurement including direct to diffuse ratio, wind speed, wind direction, barometric pressure, air temperature and relative humidity are available. A new state-of-the-art outdoor I-V measurement system capable of handling devices with a voltage and current range of ±100 V and ±40A maximum to ±0.01 mV and ±1µA minimum has become operational during FY93. A broad band spectroradiometer (300-2000 nm) that will be dedicated to this system was ordered in FY93 with delivery expected in FY 94. A second I-V system (±50V, ±16A) has been installed and is operational at SRRL. This system is part of a rating comparison project and measures the I-V characteristics of 16 modules or encapsulated cells at one minute intervals over long periods of time.

During FY93 a Large Area Laser Scanner for the micro characterization of submodules and modules became operational. The specifications and capabilities of this system are: a user selectable rectangular scan region with distance from 1 cm to over 1 m; variable laser spot size of 50 µm to over 1 mm in diameter, HeNe laser wavelength of 633 nm; variable laser power density: 1 to 100 suns; variable white light biasing from 0 to -1 sun. The system generates color coded spatial maps of the current, voltage or power versus position. This allows an electrical / optical defect map of a PV cell or module to be determined. Because the system can evaluate defects under actual operating conditions voltage and light dependent defects can be imaged.

Results
During FY 93 the team calibrated 1532 cells (I-V under standard reporting conditions), and performed over 2000 module measurements on the SPIRE 240A solar simulator (970 module measurements) and outdoors under clear sky prevailing conditions (total irradiance > 950 W/m²). These measurements were on representative cells and modules of all PV technologies being investigated at NREL, in the US and worldwide. The work of this group was acknowledged in 41 papers at the 23rd IEEE PVC, and in many more conference and journal publications. The group participated in numerous intercomparisons of PV cell and module measurements including: 1) Two international intercomparisons of conventional Si PV technologies and new R&D PV technologies sponsored by the Photovoltaic Energy Project (PEP 93); 2) An intercomparison of ASTM test methods for cells and modules; 3) An intercomparison of SPIRE 240A simulator measurements on multi-junction amorphous silicon modules with USSC, Solarex, and SPIRE; 4) An intercomparison of Si cell efficiencies organized by UNSW in Australia with participation by Sandia, the German PV calibration laboratory (ISE), and the Japanese PV calibration laboratory (JMI).

During FY 93 a new optics package was installed on the X25 solar simulator allowing samples up to 30.5 cm by 30.5 cm to be measured. The archaic HP 1000 computer system (1979 purchase date) is being phased out with the standard efficiency measurement software now residing on a Macintosh. The unrepairable cell IV measurement system control box was replaced with a better more versatile control box. A second-grating-monochrometer based spectral response system was designed and work begun to allow more accurate measurement of IR.
sensitive devices and cells with a narrow response range (for example GaAs under GaInP). The NREL Spire 240A software was modified to accommodate the new hardware and software associated with the “peak detector”. The hardware and software associated with new Standardized Outdoor Measurement System was completed and is being used for routine module measurements in FY 94. Spectral error calculations on outdoor I-V measurements can now be performed on a routine basis. For the first time ever the spectral irradiance of the Spire 240A solar simulator was measured over a wavelength interval of 300-1800 nm.

References
Objectives

The goals are to develop and demonstrate innovative flat plat PV module encapsulation materials that will provide optimum module performance and protection from the environment for a 30-year operational life in the field. The long term objectives are (1) to identify, understand, and then mitigate the causes of changes in module materials that alter crucial materials properties, reduce the performance, and/or limit the service life of the module; and (2) to develop new or improved materials that offer greater promise for a module life expectancy of 30 years.

The objectives for FY 1993 were to identify (a) new or improved materials that offer greater promise for a module life expectancy of 30 years and meet low cost goals, (b) optimal durability testing procedures, and protocol, (c) specific compatibility/durability intrinsic problems at material interfaces in cells/modules, and (d) degradation and failure mechanisms that can be used for analytical evaluation of module service life.

Technical Approach

The objectives are being addressed primarily for contemporary thin film and crystalline silicon flat plat PV module technologies. The technical approach consists of conducting experimental work, interpreting the results, establishing test methods, and seeking solutions to module reliability and materials durability problems. The background and problems associated with EVA degradation in PV modules have been summarized.1,2

For module materials and encapsulation research, generic module materials durability studies are being performed primarily on polymeric pottant materials using the recent results obtained for degraded EVA. Effort to modify the present formulation of EVA with improved UV stabilizers and thermal stabilizers was initiated, and the modified materials are being ranked from accelerated life testing (ALT) against the existing formulations (A9918, 15295, 1595P, 16718A, and 18170), all of which use Cyasorb UV 531. The materials are being subjected to both real-time testing using field deployment and ALT using DSET Suntest units, an Oriel solar simulator, and other existing light sources for test-size specimens. Designed experiments are being used to separate mechanisms thought to include UV temperature, acetic acid-catalyzed, surface catalyzed, ion catalyzed, and electric field effects. Degradation is monitored from characterization measurements made before, during, and after testing, and these emphasize UV-vis, fluorescence analysis (FA); spectrocolorimetry, high performance liquid chromatograph (HPLC), gel content, and Fourier transform infrared (FT-IR). Additional characterization
measurements are made as deemed appropriate. For metalization/semiconductor interface degradation studies, the activities focused on compatibility/durability degradation issues between the cell material/metalization interface. AES, UPS, and SIMS were used to study the SnO2/CdS interface and impurity diffusion that shunts the CdTe between the metalization/semiconductor and CdS/CdTe interfaces.

Results: Degradation of EVA in Crystalline Silicon Modules

Modified EVA and potential EVA Replacements. For modifying EVA to improve its stability, we have conducted a series of quantitative experiments to further the understanding of the stabilization effectiveness about the concentration ratio among the UV absorber (Cyasorb UV 531), UV light stabilizer (Tinuvin 770), and anti-oxidant (Naugard P). The results show that the Cyasorb UV 531 impregnated in Elvax 150 thin film can be effectively stabilized by Tinuvin 770 and Naugard P at a certain concentration ratio, whereas the photogenerated destructive free radicals are neutralized. This in-depth understanding will facilitate the development of new formulations with new stabilizers. A thin-film sample thus prepared exhibited no loss of Cyasorb after a 1000-h exposure in the Suntest CPS system at 60°C ±4°C. In the same period of time, a thin film made of the uncured A9918 showed a steadily increasing loss of Cyasorb (≥11%) and a thin film made without Tinuvin 770 and Naugard P showed a loss of ≥65%. Finally, we have continued to develop and test new formulations with new stabilizers, to acquire new stabilizers, potential encapsulation superstrate materials, and solar cells from various manufacturers for testing, and to expand the testing activities with the two new DSET Suntest CPS exposure systems and the Oriel solar simulator. A summary of FY 1993 progress is available.

Degradation Mechanisms. We have completed a series of experiments to determine quantitatively the photodecomposition rate of Cyasorb UV 531 in cyclohexane solutions as a function of light intensity. The results show that the loss rate of Cyasorb in cyclohexane solutions is non-linearly proportional to the exposure time at a given light intensity and is exponentially proportional to a linear increase of the light intensity. These results dictate that the conditions for conducting ALT shall be carefully selected or designed in such a way that the resulting degradation (rate) can be realistically related to outdoor testing.

We have elucidated the broad-based applications potential of using FA to monitor or to establish (a) the extent of EVA copolymer discoloration and degradation in field-deployed modules, (b) the extent of degradation and discoloration of other PV encapsulant polymers, (c) the structural changes of residual chromophores in EVA at various stages of processing, and (d) an understanding of structural changes occurring in exposed and/or discolored polymers. We have established that photobleaching of discolored EVA can be affected by both UV and visible light in the presence of air, which can compete with photothermal degradation of EVA. The dominant reactions are photothermal degradation at temperatures of over 85°C and photobleaching at temperatures below 50°C; at the intervening temperature the dominant reaction may be either reaction depending on the temperature, UV insolation, and other factors. Summaries of the known degradation mechanisms are available. Finally, we have demonstrated that PVB encapsulant degradation mechanisms are similar to those for EVA by using FA and
other techniques.

Efficiency Losses. We have continued or initiated several projects to monitor the efficiency losses from yellowed EVA in modules or minimodules. Details are available in reports from SWDIT and NREL.1,7

Results: Degradation in CdTe/CdS PV Modules

Stability Issues in CdTe/CdS Modules. We continued addressing stability issues in CdTe/CdS PV modules. First, we initiated studies on the formation mechanisms of SnO2/CdS interfaces and their stability in real environments. We concluded from studies of SnO2/CdS interfaces that they are surprisingly stable and resistant to environmental degradation, and that other degradation paths must account for the stability problems in CdTe/CdS modules. Summaries of this work are available.8,9

Degradation at the CdTe/CdS Interface. To identify the source of the stability problems, we acquired modules that were degraded by water vapor and subjected these to surface analysis using Auger spectroscopy and ion erosion for compositional depth analysis. By measuring I-V profiles to verify cell degradation, we determined that degraded CdS/CdTe cells have a Te deficiency near the back contact. We then showed from I-V profiles that the diode behavior of degraded CdS/CdTe modules breaks down and becomes more resistive. Copper diffusion to the CdS/CdTe interface is the suspected cause. Copper at the interface was positively identified using SIMS analysis after Auger analysis provided an unexpected anomaly that could only be attributed to Cu.

Results: Miscellaneous Related Activities

Additional laboratory equipment was purchased, installed, and used; new procedures for polymer thin film preparation, testing, and analysis were developed; and some existing equipment was repaired. Details are available.1

We completed the proceedings of a Surface Processing Workshop, which was funded by the Office of Transportation Technologies, the Office of Utility Technology (via NREL’s internal Directors Development Fund), and a small amount of other-direct-cost support from this task. The document is entitled "Current Status, Research Needs, and Opportunities in Applications to Surface Processing to Transportation and Utilities Technologies," A. W. Czanderna and A. R. Landgrebe, eds., NREL/CP-412-5007, September, 1992. Of the 10 chapters on research needs and applications, six are directly relevant to PV module durability, i.e., corrosion protection, polymer/metal (oxide) interfaces, thin-film multilayer solar collectors, accelerated life testing, interfacial microchemical characterization, and organized molecular assemblies. The document has also been published in the peer-reviewed journal, Critical Reviews in Surface Chemistry, 2 (Nos. 1-4) and 3 (No. 1), 1993.
References


Objectives

The objectives are to help improve photovoltaic module performance and reliability by developing and performing tests, establishing a correlation between indoor (accelerated) testing and outdoor (natural, real-time) exposure as related to reliability/stability/weathering issues, and by developing methods to help predict PV module service lifetime.

Technical Approach

The approach involves interacting with the PV industry (manufacturers, test facilities, end-users, etc.) to investigate and understand module long-term reliability and performance. NREL activities include developing test methods and procedures, performing exploratory module qualification tests on all commercially-available PV modules with special emphasis on thin-film technologies and test method validation, undertaking theoretical and experimental studies on PV module lifetime prediction from accelerated testing, performing and developing methods and techniques for failure analysis of PV modules including determining failure mechanisms, and developing solutions to module performance and reliability problems.

Results

Complete capabilities were made operational for conducting the tests and procedures in the Interim Qualification Tests and Procedures for Thin-Film Flat-Plate Modules document (IQT -- SERI report TR 213-3624). That includes Thermal-Cycle Test, I-V Test, Visual Inspection, and Humidity-Freeze Test, Hail Impact Test, Dry- and Wet Hi-Pot Tests, Wet Insulation-Resistance Test, Mechanical Load Tests, and Hot-Spot Tests. Interactions with industry included using the Hail Impact Test System (HITS) to test several products, prototypes, and modules, e.g., Golden Photon and Utility Power Group. The tests helped these manufacturers improve and redesign their PV modules. Additional qualification tests made operational this past year include the mechanical flex test (dynamic), scratch or surface-cut test, ground-continuity test, and saltwater immersion and corrosion test. The saltwater test was successfully run on some prototype modules from Iowa Thin-Film Technologies.

Light-Soak Test #2 was completed (Spring, 1993). It involved 17 a-Si PV modules from four manufacturers (Fuji, Iowa Thin-Film, Solarex, and USSC). The modules were exposed to ~1000 hours of one-sun illumination at 50°C, loaded at P_{max}, followed by several annealing periods at higher temperatures. The modules were then placed outdoors for further testing.
The RD-1200 Multi-Tracer (Multiplexing PV Module I-V Curve Tracer) was delivered, tested, calibrated and installed at the outdoor NREL PV test site. The multi-tracer is currently being used to obtain in-situ I-V curves of 10 PV modules from different manufacturers and various technologies including: crystalline-Si, polycrystalline-Si, CIS, and, single-, dual- and triple-junction a-Si. The multi-tracer can electrically load and measure up to 15 modules simultaneously. The computer-controlled apparatus includes a software package for calibration, control, monitoring, storing and plotting the acquired data, and obtains in-situ I-V curves for each module every 30 minutes during daylight hours, while \( V_{\text{max}} \), \( I_{\text{max}} \), irradiance, and temperature are acquired every 5 sec and averaged hourly. At present we have obtained three months of data, that is used for indoor/outdoor photostability testing, AOCS studies and the PV Energy Rating Methods (PERM) activity.

**Future Plans**

The following presents new activities and equipment capabilities planned for 1994. New module qualification tests and methods are being developed -- immersed wet hi-pot test, non-intrusive hot-spot endurance test, accelerated weathering (UV/solar radiation/thermal) test, damp heat test, and mechanical twist/termination robustness test.

A ten-month test plan has been developed for exploratory module qualification testing of commercially-available modules from various manufacturers. The first batch of modules will be run from January to May, 1994; the second batch will be run from June to October, 1994. The results will be submitted as a technical paper for presentation at the 24\textsuperscript{th} IEEE PV Specialists Conference, December, 1994. The test plan involves modules of several different PV technologies from the respective companies -- a-Si (Solarex and APS), a-Si/a-Si (UPG and USSC), a-Si/a-Si/a-SiGe (ECD), CIS (Siemens Solar), CdTe (Solar Cells, Inc.), CdTe (Golden Photon), crystalline-Si (Siemens Solar) and polycrystalline-Si (Solarex).

Light-Soak Test #3 is ready to begin with 18 contract-deliverable a-Si modules (from APS, ECD, Solarex, and USSC).

The outdoor portion of the indoor/outdoor correlation study is underway. The indoor portion will begin as soon as the light-soak testing is completed. This study will involve a comparison of the outdoor photostability of commercial a-Si PV modules with two types of indoor testing performed on identical modules -- continuous illumination and constant temperature, and cycled illumination and temperature. Our ongoing improvements in the spectrum of the Vortek argon-arc lamp should help to enhance the correlation between the indoor and outdoor results of this testing.

A reference-cell package in a module enclosure has been designed to enable us to instantaneously and simultaneously measure various portions of the incident spectrum during outdoor or indoor testing. Two of these assemblies will be used with PV systems installed at the outdoor test site, one will be used with the Standardized Outdoor Measurement System (SOMS), one will be used with the outdoor experimental test rack, and one will be used for indoor light-soak testing.
Our planned outdoor temperature-controlled test enclosure will enable PV modules to reach and maintain a desired temperature before and during measurement and testing with the SOMS apparatus. Presently, the power-driven shutter system is being designed, as well as the temperature-control system.

An irradiance/temperature chamber is being procured from Atlas Electric Devices. It will hold up to a 2' x 5' PV module, with the ability to vary the irradiance from 200-1200 W/m² and the temperature from -10°C to +90°C. This will allow us to measure the I-V characteristics of various PV modules at different illuminations and temperatures, thereby providing us with the irradiance and temperature coefficients of voltage, current, fill factor, power, and efficiency.

References


Title: PV Module and System Technology Validation

Organization: PV Module and System Performance and Engineering Project
NREL PV Program

Contributors: L. Mrig, Team Leader; T. Strand; B. Kroposki; S. Rummel; R. Hansen; and Y. Caiyem

Objectives

The objectives are to provide U.S. PV manufacturers with a test bed where emerging and maturing PV module technologies are tested and evaluated.

Technical Approach

The PV Module and System Technology Validation focus is to gather in-situ data on module and array performance, analyze that data and disseminate the results to PV manufacturers and the PV industry. That is accomplished by testing, performance evaluation, procuring and monitoring small PV systems and the NREL Solar Energy Research Facility (SERF) PV systems, and participating in development of PV standards and codes. Activities include installing and monitoring individual modules as well as small PV systems at NREL’s Outdoor Test Site. The types of systems deployed range from stand-alone systems feeding maximum power or fixed resistance loads, to utility grid interconnected systems employing DC to AC inverters.

Participation in PV module and system consensus standards development includes Institute of Electrical and Electronic Engineers (IEEE - SCC21 Committee), and managing the NREL subcontracts for IEC TC-82 secretariat, U.S. technical advisory group coordination of international PV standards development, and coordination of revisions to the National Electrical Code (NEC) Article 690 for PV systems. These activities emphasize developing consensus qualification testing, energy rating and safety standards.

Capabilities and facilities at NREL in support of the validation efforts include PV system design, PV system modeling, PV system analysis, PV system monitoring, PV system instrumentation, power quality measurements (THD), outdoor module IV traces (Hewlett Packard/SOMS), indoor module IV traces (SPIRE), array/string IV traces (Daystar), and five array structures that are capable of hosting utility grid interconnected PV systems.

Results

The NREL Sixth Photovoltaic Performance and Reliability Workshop [1] was sponsored and coordinated under this task area. One-hundred-nineteen attendees participated in the workshop held in Golden, CO, on September 8-10, 1993. Thirty-five speakers discussed various technical issues in the five technical sessions (i) Cell and Module Characterization, (ii) Module and System
Testing, (iii) Durability and Reliability, (iv) Field Experiences, and (v) Standards and Codes. Panel discussions were held after each session which generated open dialogue among the audience and panel members. Over 40 attendees toured the NREL PV outdoor test facilities, and the module accelerated test and cell characterization labs.

During the 1993 PV Standards and Codes Forum sponsored and held at NREL on June 14-16, 1993, the members of ASTM, IEEE and the US/IEC TC82 PV standards committees reviewed the IEEE SCC21 draft document (version 3) entitled Recommended Practice for Qualification of Photovoltaic (PV) Modules, a comprehensive qualification test document for flat-plate modules. This document development is being led by NREL engineers.

Additional accomplishments under this research area included:
- Deployed the United Solar Systems Corporation 1 kW roofing array.
- Deployed the Siemens Solar Industries 1 kW CIS array.
- Deployed/instrumented Brazilian Rural Electrification Pilot Project stand alone lighting systems.
- Provided an Interim Test Report evaluating the Brazilian Project systems, and provided a Corrective Action Report for that system.
- Designed and constructed an Area Lighting Test Bed.
- Completed the system requirements and RFP for the NREL SERF PV Systems.
- Conducted a Field Evaluation of the 10,000 Trees PV Project 2.5 kW Solar Electric Pump Irrigation System (PSCo and the City of Littleton, CO).
- Supported the installation of six commercially available area lighting systems at NREL for testing.
- Installed Mobil Solar Energy Corporation poly-crystalline silicon modules for monitoring as part of the PVUSA Project.
- Installed one Siemens Solar CIS module for correlating performance data between module and system performance.
- Installed Solar Cells Inc. CdTe modules for stability evaluation.
- Installed an enclosed resistor box for the CIS module rack.
- Started Process of converting HP 300 Data Acquisition System (DAS) to a DOS format DAS.
- Installed a LICOR LI-1776 Solar Monitor at NREL in Trailer 6305. This monitors the total kWh/m² of solar radiation at a 40° tilt. This data is being used in the light soak 3 outdoor test.
- Draft version 4 of the IEEE SCC21, "Recommended Practice for Qualification of Photovoltaic Modules" document was completed and released to reviewers.
- Stability tests conducted on a-Si, CIS, and CdTe modules and results were reported.
Future Plans

- Provide Technical Report on the USSC 1.8 kW utility grid interconnect PV system (Mar 94).
- Support PVUSA/EMT projects.
- Design/install 4 grid connected PV systems
- Sponsor and hold the NREL Seventh Photovoltaic Performance and Reliability Workshop and contribute to the 1994 PV Standards and Codes Forum.

References


2. *Installation and Preliminary Evaluation of Six Photovoltaic Stand-Alone Area Lighting Systems*, Troy Strand and Peter McNutt, 12th NREL PV Program Review Meeting October 14, 1993


Objectives

The photovoltaic Solar Radiation Research (SRR) team provides scientific understanding of incident natural and artificial illumination, supporting characterization and performance testing of PV cells, modules, and systems. Emphasis is upon development and use of radiometric instrumentation systems, measurement techniques, and calibrations to reduce uncertainty in PV device and system performance testing and evaluation. The team addresses broadband (300 nanometers [nm] to 2400 nm) and spectral (wavelength dependent) radiometric measurements required to characterize artificial and natural illumination sources for PV reference standards, prototype, and commercially available PV devices tested within the PV Module and System Performance and Engineering Project and for other NREL PV Program participants. The team exchanges technical information with industry and NREL PV engineers and researchers concerning radiometric measurements, instrumentation, analysis, and PV solar radiation resource data.

Technical Approach

Radiometric calibrations are performed in the Optical Metrology Laboratory, shared with NREL’s Metrology Laboratory. Spectral and total irradiance reference standard sources purchased directly from the National Institute of Standards and Technology (NIST), and quality electronic equipment support improved radiometer calibration and measurement techniques.

Routine and specialized spectral and broadband optical radiometric instrumentation is calibrated, maintained, loaned, and operated to provide solutions to measurement needs of NREL internal and external PV Program participants. NREL researchers, engineers, and subcontractors obtain technical consultation on radiometric measurement problems and data analysis or interpretation critical to PV performance calibrations, testing, and evaluation. This includes measurements using the NREL Atmospheric Optical Calibration System (AOCS) to monitor differences in atmospheric parameters with respect to standard reporting conditions during outdoor testing.[1,2,3]

Team personnel provide unique technical experience addressing NREL PV related optical radiometric measurement needs by maintaining state-of-the-art optical metrology instrumentation and capabilities. To keep abreast and contribute to this field, team members participate actively in organizations such as the Council for Optical Radiation Measurements (CORM), the Society of Photo-Optical and Instrumentation Engineers (SPIE), and the NIST Radiometric Physics Division. T. Cannon is a member of the CORM board of directors.
Results

Accomplishments of the team during fiscal year (FY) 1993 include the following:

- Developed, tested, calibrated and used the NREL Pulse Analysis Spectroradiometer System (PASS) instrumentation to measure spectral distribution of NREL’s SPIRE 240A pulsed solar simulator, providing the first ever ability to quantify spectral errors for multijunction module sized devices tested under this source. [4,5]

- Measured the spectral content (300 nm to 2400 nm) of NREL’s PV Efficiency Measurements task X-25 solar simulator and NREL’s PV Module Qualification Testing task VORTEK simulator; providing information on lamp stability and spectral error sources.

- Provided eleven broadband and five spectral instrument calibrations, in collaboration with the NREL Metrology Service Center.

- Specified and procured instrumentation for reference solar irradiance and meteorological data, with installation planned for early FY 1994.

- Converted the Atmospheric Optical Calibration System (AOCS) software and hardware to IBM-compatible platform, and collected AOCS data at the NREL test site. Study of correlations of AOCS data and automated PV performance data (periodic current-voltage curve tracing) for 6 different PV technologies is underway.[5]

- Collected a second site-year of solar resource data for the Public Service Company of Colorado (PSCo) at the Fort St. Vrain generating plant in Platteville, CO.

- Collaborated with NREL’s Technology and Resource Assessment Branch (C. Riordan, T. Stoffel, B. Marion) and the Solar Radiation Resource Assessment Project (SRRAP) to contribute to the following results:

  - Assessment of resources for the PSCo Valmont generating plant in Boulder, CO., based upon the National Solar Radiation Data Base (NSRDB) and Fort St. Vrain generating plant solar monitoring data measured by the task for 1991-1992.

  - A new Solar Radiation Data Manual for Flat Plate and Concentrating Collectors based on NSRDB data. This publication provides monthly extremes and summaries of solar resources and meteorological data for 14 collector types at all 256 sites within the NSRDB. The manual will be published in mid FY 1994 [6].

Table 1 is a partial list of SRR interactions and technical information transfer in FY 1993.
TABLE 1. Examples of SRR External Interactions, FY 1993

| Utilities | Electric Power Research Institute  
| Public Service Co. of Colorado |
| Industry | Ascension Technology, Inc.  
| Atlas Corporation  
| DSET Laboratories, Inc.  
| Eppley Laboratory  
| Optronics Laboratories  
| Texas Instruments, Inc. Solar Program  
| United Solar Systems Corporation |
| Educational Institutions | Iowa State University  
| State University of New York, Albany  
| Wayne State University |
| State and National Laboratories | NIST  
| International Energy Agency  
| World Meteorological Organization |
| Professional Organizations | Institute of Electrical & Electronic Engineers  
| Council for Optical Radiation Measurements  
| Society for Photo-optical Instrumentation Engineers |

Conclusions

The PV test engineers conducting performance, stability, and system monitoring activities at the NREL PV outdoor test site will be able to compare plane of array (POA) radiometric data with high quality site representative data from the Reference Meteorological and Irradiance System (RMIS). The SRR team will operate, maintain, and calibrate the components of the RMIS, and archive 1 minute time resolution data for future analysis and correlation studies. Routine calibrations of plane-of-array sensors will be co-ordinated by the PV-SRR team, giving traceability and uncertainty for POA measurements at NREL.

Unique measurement instrumentation and techniques have produced spectral content data for the NREL SPIRE 240A. This has permitted the examination of spectral error effects which impact the multijunction and amorphous silicon PV technologies. Future work includes the characterization of differences between simulators and simulator types, such as large area continuous simulators and Large Area Pulse Solar Simulators (LAPSS). The SRR team will maintain an on-call measurement capability for existing and future solar simulators.

Interpretation of outdoor PV performance data collected under prevailing conditions can be accomplished by correlating AOCS and PV performance data. Future work includes integration of real time spectral error correction routines to quantify spectral errors as a function of AOCS parameters, and integration of AOCS parameters into the Reference Meteorological and Irradiance Station data distribution to ongoing PV performance testing.
References


Objectives

The objective is to provide coordination for developing PV standards, codes, and criteria for test and evaluation procedures that are consistent with the DOE National Photovoltaic Program.

Technical Approach

Technical approaches used for these objectives included participation with the IEEE Standard Coordination Committee 21, and chairing ASTM subcommittee E44.09, titled Photovoltaic Electric Power Systems. Emphasis was also placed on developing criteria for module certification (emphasizing qualification testing) and test facility accreditation with the PV community through a consensus approach (review committee) with balanced industry representation and subcontract support. Other efforts included coordination and initiation of the PEP’93 Intercomparison of reference cell calibrations and cell performance measurements, and coordination of the ASTM cell and module measurement round-robin. To facilitate these activities, it was desired to convene a PV Standards and Codes Forum to hold individual and joint meetings at the same location and establish coordination of efforts and flow of information between committees on standards issues.

Results

The PEP’93 Intercomparison coordination effort began with the 1st Participants’ Meeting that was coordinated and lead by C. Osterwald during the 11th European PV Solar Energy Conference and Exhibition which was held in Montreux, Switzerland in October 1992. This meeting, which was attended by representatives from major international PV laboratories, established the objectives, sample set, calibration methods, and schedule for the intercomparison to begin in July 1993, which is the first to include laboratories from outside the PEP member nations. Two separate sample sets will be circulated. The first is composed entirely of 2x2 cm single-crystal Si reference cells that each participant will calibrate with their best calibration method. The results of these calibrations will be analyzed and used to establish the World PV Scale (WPVS) of primary reference cells. The second sample set consists of devices from newer PV technologies that have unique measurement problems, such as narrow bandgap cells, large-area cells, and series-connected tandem cells. Twelve laboratories from throughout the world agreed to participate. Each participant is assigned two months to complete measurements for each sample set, and the sample circulation is scheduled to be finished on June 30, 1995. A second participants’ meeting during the 23rd IEEE PVSC in Louisville, Kentucky in May 1993
finalized the schedule and sample sets. The sample sets were assembled and pre-tested at NREL, and were delivered on time to the first scheduled participants by July 1, 1993.

PV standards activities within ASTM during FY 1993 dealt with several issues of importance to the PV industry. At the November 1992 meeting of subcommittee E44.09, chaired by C. Osterwald, Heraeus (DSET Labs) presented a revision of the draft standard for solar UV weathering of PV modules which the subcommittee has been working on for over seven years, which draws on the extensive experience of existing standards on solar UV weathering for materials. These standards are important because they have shown correlation between real-time outdoor and accelerated indoor exposure. Because of the issue of EVA degradation discussed by the PV community for the past several years, the length of exposure was the last remaining technical detail to be surmounted before the draft could begin the ASTM balloting procedures. This test method was changed to a time-to-failure from an arbitrary fixed-duration UV exposure procedure. Work was also completed on a draft test method for saltwater PIT (Pressure-Immersion-Temperature) cycling of PV modules. This test method was developed by the U.S. Coast Guard for their offshore buoy PV systems, who initiated development of the draft. It is anticipated that both of these test methods will be approved as ASTM standards by mid-1994.

Another E44.09 draft standard for wet insulation integrity testing of PV modules was reviewed and the subcommittee decided to change this test to a full-immersion only (no spraying) procedure. The issue of module wet insulation integrity testing is also of interest in IEEE SCC 21, which has been developing a full qualification sequence standard for modules.

A task group of E44.09 was formed in June 1993 to consider development of a new standard for performance and spectral response testing of multi-junction PV devices. At a subsequent meeting in September 1993, the task group decided that standardization for multi-junction measurements is important and that an outline of a new draft test method should be written.

During 1993 several new and revised E44.09 standards were approved, including: E 1038, Test Method for Determining Resistance of Photovoltaic Modules to Hail by Impact with Propelled Ice Balls; E 1040, Specification for Physical Characteristics of Non-concentrator Terrestrial Photovoltaic Reference Cells; E 1171, Test Method for Photovoltaic Modules in Cyclic Temperature and Humidity Environments; and E 1524, Test Method for Saltwater Immersion and Corrosion Testing of Photovoltaic Modules for Marine Environments.

Circulation of the sample set for the ASTM cell and module measurement intercomparison continued through May 1993, with a total of six US PV laboratories completing the measurements. The intent of the intercomparison is to provide measurement error information, required by ASTM, for several existing E44.09 standards. These standards cover measurement of cell and module performance, cell spectral response, and reference cell calibration. Preliminary results from the intercomparison were presented at the 23rd IEEE PVSC in May 1993 [1]. Circulation among the remaining participants halted when the samples were misplaced at one facility.

The module certification and laboratory accreditation was begun with the issuance of a Request for Proposals (RFQ), titled Photovoltaic Module Certification / Laboratory Accreditation Criteria.
Development. The major deliverable for this subcontract will be to develop and document criteria and recommendations that specify guidelines to be used to certify a PV module for performance and reliability, along with the specific equipment, facilities, quality assurance procedures, and technical expertise an accredited laboratory needs in order to perform PV module certification. Development of the criteria and the documentation will take place through a consensus committee of representatives of PV manufacturers, end users, standards and codes organizations, and testing laboratories. The awardee will coordinate the committee activities and criteria development, which will ultimately be published as an NREL technical report for use by the PV community. Three proposals were received in response to the RFQ, and the proposals were reviewed by the source evaluation panel formed at NREL. It was anticipated that an award would be made early in FY 1994.

On June 14-16, 1993, the first PV Standards & Codes Forum was held at NREL. This meeting included a 1/2 day forum that featured introductions and overviews of the US standards and codes activities, and a panel discussion of needs, problems, and directions of standards activities. Each of the three US standards groups then held 1/2 day meetings in succession. A full day was devoted to working groups that spent time on new standards development. The forum had a total attendance of 36 representatives from throughout the PV industry. Highlights of the meeting included initiation of work on a new document for PV safety that will also be used as inputs for possible changes to the National Electrical Code that are needed for installation of non-utility PV systems. There was a major discussion of dry and wet PV module insulation testing that spanned both the ASTM E44.09 PV subcommittee meeting and the working group of IEEE SCC 21 working on development of a module qualification sequence standard. The US Technical Advisory Group to IEC Technical Committee 82 (international PV standards) also met and presented the results of the May 1993 TC82 meeting in Ischia, Italy.

Conclusions

The objectives were successfully met as evidenced by the following summary of significant accomplishments: chaired and coordinated PEP'93 reference cell comparison at first meeting Montreux, Switzerland (meeting, 10/92); published results of ASTM interlaboratory cell/module round-robin testing (5/93); and organized and led a PV Standards and Codes Coordination Forum that included consensus standards and codes organizations (6/93).

Progress in ASTM E44.09 standards development was encouraging as several new and revised standards were completed. The PEP'93 Intercomparison is a major new effort as it is the first to include laboratories from outside the PEP member nations. This important new work was successfully initiated and should provide valuable data on the state of PV measurements worldwide, and give for the first time, a World PV Scale for PV performance.

References

Objective

The objectives of the project are 1) to assist in the development and qualification of utility-scale amorphous silicon photovoltaic modules, 2) to improve the reliability of utility-scale amorphous silicon modules and utility grid-connected systems, 3) to demonstrate potential markets for amorphous silicon photovoltaic modules and systems, and 4) to form utility/manufacturer/user teams to promote photovoltaics within the utility sector.

Technical Approach

Amorphous silicon photovoltaic technology has a significant potential for reducing the cost of photovoltaics from today's costs. Before that potential is realized, newer modules must be developed and validated in systems. Module development coupled with system integration reinforces the need to consider the system as a whole. Under this project, competitive subcontracts were awarded consisting of Phase 1 for module development and qualification and Phase 2 for system design, deployment, and monitoring. In some subcontracts the system design is part of Phase 1.

For Phase 1 module performance goals are based on stabilized performance not initial performance. Amorphous silicon photovoltaic modules exhibit an initial 15-30% decrease in power within the first two months of system deployment. After this initial power decrease the performance appears to stabilize. The stabilized module power output is defined as the power output measured under standard test conditions after the module has been exposed to 1000 W/m² of nominally white light at a module temperature of 50°C and under a fixed resistive load. The stabilized power output is a better indicator of future performance than the initial power output. Also, modules developed for Phase 1 must pass NREL's "Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules" (SERI/TR-213-3624). Design reviews of the proposed systems will take advantage of the expertise at NREL, Sandia National Laboratory, and the PVUSA Project.
For Phase 2 the modules will be deployed in grid-connected systems ranging from 3.4 kWp(ac) to 50 kWp(ac). The performance of the system will be determined after 60 days of operation. Performance will be monitored by a data acquisition system supplied by the PVUSA Project. NREL will monitor the performance and the data will be shared with the photovoltaic manufacturer, the utility, and PVUSA.

Results

A Request for Proposal (RF-1-11061) was issued in 1991 and all awards were completed in 1993. Awards were made to Advanced Photovoltaic Systems, Energy Conversion Devices, Energy Photovoltaics, Integrated Power Corporation, Solarex, and Utility Power Group.

Results: Energy Conversion Devices

Subcontract AI-2-11061-1 was awarded to Energy Conversion Devices, Troy, Michigan. The objectives are to develop triple-junction amorphous silicon photovoltaic modules with a 7% average stabilized total-area efficiency, certify that these modules pass NREL's Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules, and deploy these modules in a 10 kWp(ac) system. During Phase 1, ECD will develop triple-junction amorphous silicon photovoltaic modules with dimensions of approximately 34 cm by 126 cm and certify that these modules have passed NREL's Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules. In FY 1993 ECD delivered four modules for light-soaking with an 8.0% average initial total-area efficiency. Phase 2 is negotiated to design and install a 10 kWp(ac) system on the Auburn Hills Campus of Oakland Community College in Oakland, Michigan.

Results: Solarex

Subcontract AI-3-11061-2 was awarded to Solarex Thin Film Division. The objectives are to develop triple-junction amorphous silicon photovoltaic modules with a 7% average stabilized total-area efficiency, certify that these modules pass NREL's Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules, and deploy these modules in three systems totalling 10.2 kWp(ac). Phase 1 is negotiated to develop triple-junction amorphous silicon modules with dimensions of approximately 30 cm by 90 cm and certify that these modules have passed NREL's Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules. During Phase 1 Solarex has sent two modules with an average initial total-area efficiency of 6.2%. Phase 2 is negotiated to design and install three 3.4 kWp(ac) systems in the service territory of the Salt River Project and Arizona Public Service. The three systems will be designed to assess the performance of triple-junction modules in a sunny, hot climate with three different mounting configurations.
Results: Integrated Power Corporation

Subcontract AI-2-11061-3 was awarded to Integrated Power Corporation, Rockville, Maryland. During Phase 1, IPC delivered 4 modules (UPM-880) from United Solar Systems Corporation that NREL light soaked for 600 hours at 50°C under nominally white light of 1000 W/m². Measured under standard conditions, the average power output of the four light-soaked modules was 21.5 W, which was within measurement error of the goal of 22 W per module. USSC certified that these modules passed NREL’s Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules. IPC installed the system on the roof of a New York Transit Authority warehouse in Maspeth, New York. The system uses a unique ballast-weighted configuration using precast concrete curbs that avoids the need to penetrate the roofing membrane. The PV system became operational on June 18, 1993. After 60 days of operation, the system was rated at 17 kW(ac) which is greater than the contractual requirement of 15 kW(ac). Data are routinely collected on system performance. A paper on the "Design Considerations and Performance of Maspeth a-Si System" was presented at the 12th NREL PV Program Review Meeting [1].

Results: Energy Photovoltaics

Subcontract AI-3-11061-4 was awarded to Energy Photovoltaics, Princeton, New Jersey. The objectives are to develop amorphous silicon photovoltaic modules with a 6.2% average stabilized total-area efficiency, certify that these modules pass NREL’s Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules, and deploy these modules in three 10 kWp(ac) systems. During Phase 1, EPV will develop amorphous silicon modules with dimensions of approximately 30 cm by 90 cm, certify that these modules have passed NREL’s Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules, and design three 10 kWp(ac) system using these modules. EPV is building the necessary module manufacturing equipment and has not yet sent any PV modules. Phase 2 is negotiated to install three 10 kWp(ac) systems in the service territory of Florida Power Corporation, GPU Service Corporation, and the City of Santa Clara, California.

Results: Utility Power Group

Subcontract AI-3-11061-5 was awarded to Utility Power Group, Chatsworth, California. The objectives are to develop amorphous silicon photovoltaic modules with a 6.3% average stabilized total-area efficiency, certify that these modules pass NREL’s Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules, and deploy these modules in a 20 kWp(ac) system. During Phase 1, UPG will develop amorphous silicon modules with dimensions of approximately 33 cm by 37 cm and certify that these modules have passed NREL’s Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules. UPG has sent two intermediate module deliverables with an average initial total-area efficiency of 6.3%. Phase 2 is negotiated to design and install a 20 kWp(ac) system in the service territory of the Los Angeles Department of Water and Power.
Results: Advanced Photovoltaic Systems

Subcontract AI-3-11061-6 was awarded to Advanced Photovoltaic Systems, Princeton, New Jersey. The objectives are to develop amorphous silicon photovoltaic modules with an average stabilized power output of 63.5 W, certify that these modules pass NREL's Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules, and deploy these modules in a 50 kWp(ac) system. Phase 1 is negotiated to develop 63.5 W amorphous silicon modules with a total area of approximately 1.2 m², certify that these modules have passed NREL's Interim Qualification Tests and Procedures for Terrestrial Photovoltaic Thin-Film Flat-Plate Modules, and submit a preliminary design for a 50 kWp(ac) system using these modules. During Phase 1 APS has sent two modules with an average initial power output of 75 W. Phase 2 is negotiated to complete the design and install a 50 kWp(ac) system in the service territory of Public Service Company of Colorado near the decommissioned Fort Saint Vrain nuclear power plant.

References

Title: Photovoltaic Power Systems for the Solar Energy Research Facility

Organization: Bechtel Corporation

Contributors: National Renewable Research Laboratory, Bechtel Corporation Research and Development, Siemens Solar Industries, Omnion Power Engineering and miscellaneous equipment suppliers

Objectives

The newest building in the NREL facilities is the Solar Energy Research Laboratory. NREL approved a project to add a 6 kW photovoltaic system each to the east and west wings of the SERF building. These two systems will connect to the Public Service Company of Colorado power grid via the electrical distribution systems of the SERF building.

Technical Approach

Competitive proposals were solicited for photovoltaic systems which used proven components and conformed to the requirements of the utility company. Selection was based on the technical quality, price, and a general appearance compatible with the building architectural theme and the high quality of the SERF laboratory.

Results

The matching systems which will be installed on the east and west wings of the SERF building utilize SSI M55 Series Cz-Si modules arranged in 20 panels (of 7 modules each) on both roofs. The ac output is at 120 volts single phase. Transducers provide signal outputs reporting system DC volts, DC amps and AC kW output.

Conclusions

Evaluation of the system and its contribution to, and impact on, the building electrical distribution system will require several months of operating experience. Additional instrumentation will be needed to collect an adequate data set for evaluation.

References

NREL subcontract No. AAN-3-1330C-1 "Photovoltaic Power Systems for Solar Energy Research Facility" including modifications 1 and 2.
Title: One kilo-Watt CdTe Photovoltaic System

Organization: Solar Cells, Inc.
Toledo, Ohio


Objectives

The objective of this subcontract is to install a 1 kW photovoltaic array and DC combiner box at NREL, and monitor and report the array performance.

Technical Approach

The 1 kW photovoltaic array consists of twenty-four 60 cm x 120 cm thin film CdTe modules. Four modules are wired in series and the six strings are run to the DC combiner box. The DC combiner box collects the input from the six strings and outputs it to a grid connected inverter.

Results

The DC combiner box has been built and installed. The panels have not yet been manufactured.
Objectives

SEIA in conjunction with NREL identified a need to increase the participation of members of the PV Industry in the development of standards and codes. SEIA also considered it necessary to directly facilitate and participate in the ongoing development of standards and codes by such bodies as IEEE SCC-21 and the NFPA’s Code Making Panel (CMP) #3.

Technical Approach

Various approaches have been used to achieve the goals of the project. By far the most effective have been committee meetings involving PV Industry, the National Laboratories, utilities, regulators, and those developing standards and codes.

To increase information flow and industrial participation in the standards and codes process, SEIA has convened a standing subcommittee on standards and codes. The committee is comprised of a diverse representation from the PV Industry as well as the National Laboratories and representatives to the standards community from the PV Industry.

SEIA has also used questionnaires, letters of inquiry, and ad-hoc meetings in its effort to ascertain the PV industry position on various issues.

Results

The National Fire Protection Association has sanctioned a task group consisting of representatives from SEIA, NREL, Sandia, and the PV industry to review Article 690 of the National Electrical Code and present its findings and recommendations for the 1999 code cycle. As part of this effort SEIA has formed a Technical Review Committee (TRC). The participants of the TRC have formed working groups to address specific issues related to the review of Article 690.

The IEEE standards developing body for Photovoltaics, SCC-21, has started work on a Safety Guideline for Terrestrial Photovoltaic Systems at the request of those working on the NEC effort to give technical substantiation to their recommendations where needed.
Conclusions

Within the last year SEIA in conjunction with NREL has been able to increase the participation of the PV Industry in the standards and codes process. Channels for communication between the two communities have also been expanded.

Of great importance to the industry as a whole is the two-and-a-half year review of the National Electrical Code. The results of this review will hopefully effect the NEC in such a way as to facilitate the increased acceptance and usage of photovoltaics.

References

Title: National and International Photovoltaic Standards Development


Contributors: R.J. Klein, Program Manager; R. DeBlasio; L. Mrig; R. D'Aiello; S. Chalmers; J. Anderson; J. Wohlgemuth; D. Feder; C. Whitaker. In addition, all experts that comprise IEEE Standards Coordinating Committee (SCC) 21, Photovoltaics; United States Technical Advisory Group (USTAG) that is responsible for United States input into the international arena; ASTM Committee E44.09, PV Electric Power Systems, members serving as a team to assist in the development of the PV standards.

Objectives

The objective is to transfer technology of photovoltaic modules, balance of systems, components and services.

Technical Approach

The approach is to draft national and international standards that can be used by both industrialized and the emerging third world nations. Such standards should reduce product cost, increase product performance and open larger world markets for the photovoltaic and related industries.

This is pursued by performing the secretariat duties for the International Electrotechnical Commission (IEC) Technical Committee 82, Solar Photovoltaic Energy Systems. This maintains continuity of current and future activities through the IEEE/SCC21, ASTM committee E44.09, and the USTAG.

Results

In FY 1993, activities included the IEEE/SCC21 having met three times. One meeting was held at Underwriters Laboratories Inc., (UL) where the committee discussed and suggested technical additions to a IEEE/SCC21 draft that addresses "Qualification of Photovoltaic (PV) Modules." Three new project authorization requests (PAR) have been submitted to the IEEE Standards Board.

A photovoltaic standards and codes forum was held at the National Renewable Energy Laboratory (NREL). Overviews were presented on IEEE/SCC21, the NEC photovoltaic activity, ASTM E44.09 and the USTAG for IEC/TC82 affairs.
The USTAG held three meetings during FY 1993 and supplied five experts for participation in the international standards writing committee meetings. The committed Secretariat support was also supplied for the Technical Committee 82 plenary session held in Ischia, Italy. One result of that meeting was that an utility interface standard was approved for circulation as a final committee draft for vote. Several other new work item proposals were also accepted and the glossary working group was reinstated.

National Standards Published


- IEEE 1144, Recommended Practice for Sizing Nickel/Cadmium Batteries for Photovoltaic (PV) Systems. Note: This standard has passed all committee approvals and IEEE required coordination. It must yet be final approved by the IEEE Standards Board.

International Standards Published

- IEC 1194, Characteristic Parameters of Photovoltaic (PV) Systems.

- IEC 1215, Design Qualification and Type Approval of Crystalline Silicon Terrestrial Photovoltaic (PV) Modules.

Future Plans

If approved by the IEEE Standards Board, the IEEE SCC21 Committee will draft standards that address the following:

- IEEE recommended practice for determining performance characteristics and suitability of a battery in a photovoltaic system.

- IEEE guide for terrestrial photovoltaic power system safety. The contents of this publication could be used and serve as a basis to suggest changes in the National Electric Code (NEC) to improve the applicability of the code to photovoltaics, and

- IEEE recommended practice for field test methods and procedures for grid-connected photovoltaic systems.
Objectives

The objective of this subcontract is to supply components and technical support for a turnkey 1.8 kW (peak) grid-connected PV system of USSC dual-junction amorphous silicon modules (UPM-880). USSC will supply the modules, interconnection wiring, diodes, combiner box, Omnion inverter (2 kW), data acquisition system, and O&M manual.

Technical Approach

NREL coordinated the design of the system. NREL also installed the array and balance of system components as well as utility interconnection with the Public Service Company of Colorado power grid.

Results

NREL successfully completed the system installation and start-up at NREL's outdoor test site, and has been monitoring the performance of the PV system since December 1992. The system performance is being continuously monitored by NREL personnel and data are being supplied to USSC for their use in understanding the performance of the system. The system performance was reported at the Sixth PV Performance and Reliability Workshop and the 1993 NREL PV Program Review meeting.

Conclusions

This subcontract has been successfully completed and the subcontract was closed out in FY 1993.

References

Objectives

The goals of this subcontracted work are (i) to conduct a methodical evaluation of potential PV module encapsulants to replace EVA, and (ii) to formulate, prepare, and deliver for test modified Elvax 150 (the principal ingredient in EVA) with different UV absorber-stabilizer combinations and other appropriate ingredients for enhancing the stability, processibility, polymer initiation, and other needs as determined by its intended use in PV modules.

Results: Identify and Recommend Modified EVA Formulations

Ethylene-vinyl acetate (EVA) copolymers currently used for photovoltaic (PV) cells have exhibited evidence of long term degradation that is detrimental to the efficiency of the PV modules. It is thought that this degradation is catalyzed by ultraviolet (UV) light as well as thermal energy and is also enhanced by the presence of acetic acid and the metal at the surface of the polymer. The first two and a half months of this work, as proposed, have focused on identifying the mechanisms by which EVA copolymers degrade, determining the possible success of stabilizers and UV absorbers, and preliminarily evaluating alternative materials.

With regard to identification of the EVA degradation mechanism, a number of outstanding studies have been found and studied in which degradation mechanisms are examined. Several conclusions are easily obtained from the composite of these studies. First, the presence of oxygen in the EVA sample (even minute amounts of dissolved oxygen), particularly at elevated temperatures will catalyze the degradation of the EVA into acetic acid at relatively high rates. Second, as is already known by those at NREL, there is a definite combinatorial effect between the radiative and thermal degradation pathways. This effect leads to much more rapid degradation of the EVA when in the presence of both UV and thermal energy as compared to the effects of either UV energy or thermal energy on their own. Lastly, all or nearly all of the EVA degradation pathways are autoaccelerative in nature. This fact implies that the greater the EVA degradation, the more rapidly further degradation will take place.

It is this problem with autoaccelerative EVA degradation that leads us to our conclusions regarding the efficacy of stabilizers and UV absorbers. The incorporation of stabilizers and UV absorbers will, with the selection of the appropriate combination, significantly retard the EVA degradation. However, when one is attempting to produce a material that will maintain 90% of the output efficiency for 20 to 30 years after installation, retardation and cessation are not equivalent.
During the lamination process, temperatures of significantly greater than 100°C are used and maintained for extended periods of time. Near these temperatures, thermogravimetric studies have shown that EVA will rapidly degrade into acetic acid and other products. These reactions have also been shown to be sensitive to the presence of oxygen (which increases the production of acetic acid). Without studies of the stabilized system, it is unlikely that even a stabilized system would not degrade to a significant extent during this lamination process. Recalling that the degradation mechanisms are generally autoaccelerative, it is thought that the degradation that occurs during lamination will catalyze further degradation, which the stabilizers and UV absorbers will not be able to inhibit entirely.

From the survey of the literature, several suggestions are apparent that might result in an improved stability and durability by altering the processing conditions rather than the formulation. Alterations to the processing conditions should include the removal of all oxygen from the curing environment and from the EVA sample itself during processing and if possible the use of lower curing temperatures to prevent initial degradation. These suggestions are designed to minimize the amount of initial degradation that occurs because of the processing conditions. EVA is partially degraded at elevated temperatures and the degradation is significantly enhanced by oxygen. These changes are likely to be both beneficial and easily incorporated as well as evaluated.

With respect to other formulations, the stabilization of an EVA film is difficult at best because it is thin and strongly absorbs UV light. As discussed in a summary of protective agents for stabilizing polymers, either of these factors make it difficult to stabilize a polymer. The fact that the sample is thin and strongly absorbing does not easily allow for the presence of an absorber/stabilizer that will quickly reduce the UV light intensity. With these limitations in mind and the additional requirement of solubility in the polymer, it is recommended that the EVA stabilized with Hostavin N20 (manufactured by Hoechst Celanese) be compared to EVA stabilized by Cyasorb 531.

Finally, a list of other materials suggested as possible replacements for EVA has been accumulated. The suggestions include polyvinyl chloride, polystyrene, polyesters, polyvinyl alcohol, acrylics, etc. This list was previously developed by the Jet Propulsion Laboratory and narrowed from cost and optical transparency concerns to two liquid polymerizable systems (butyl acrylate and aliphatic urethanes) as well as an additional laminatable polymer, poly (ethylene-co-methyl acrylate).

**Future Plans**

The literature will be further used to accumulate a thorough list of the possible stabilizers and UV absorbers that are available as well as the stabilization mechanism for each of these. Evaluation of the suggested alternative materials will be performed, and further work on identification of other, improved alternatives will be carried out.

In coordination with NREL staff we will prepare and characterize at least four of the recommended formulations identified for accelerated, abbreviated, or other testing followed by characterization at NREL. The subcontract is expected to end mid-1994.
7.0 PV ANALYSIS AND APPLICATIONS DEVELOPMENT PROJECT

Roger W. Taylor (Manager)

During FY 1993 activities included in-house investigations and management of subcontracted efforts (both through NREL and in support of DOE GO) that supported several broad analysis, market, and applications development areas, including: Solar 2000, PV-DSM analysis, solar/utility load matching, PV in buildings (PV:BONUS), PV for electric vehicle recharging, Sunrayce '93, Soltech '93, and support of state PV collaborative and regulatory interfaces, including the Utility PV Group. Major attention was placed on implementation of the Joint U.S./Brazilian Renewable Energy Rural Electrification Pilot Project during FY93, with completion of Phase 1 contracting, installation of Phase 1 hardware, and planning and initiation of Phase 2 activities which will expand DOE/NREL involvement in Brazil from two states to seven.

The PV Analysis and Applications Development Project brings together a small group of senior NREL PV personnel to focus increasing attention on the growing analytical, applications, and market development needs of the DOE PV Program and the DOE Office of Solar Energy Conversion.

During FY 1993, NREL subcontract activities included four significant efforts as follows:

- Solar Resource, Utility Load Matching Assessment; SUNY-Albany
- Evaluation of DSM Incentive Opportunities for PV; University of Delaware
- Design for Photovoltaics: Curriculum Development for North American Architecture School Faculty; AIA/ACSA Research Council
- Brazilian Rural Electrification Pilot Project; Siemens Solar Industries and Centro de Pesquisas de Energia Eletrica (CEPEL).

In addition to these subcontracts funded directly by NREL, this project has supported the development and implementation of grants and cooperative agreements administered by the DOE Golden Field Office (GO) that provide funding for U.S. PV market development activities through the new Utility PV Group and the Solar Energy Research and Education Foundation, as well as the PV:BONUS (PV-Buildings) initiative.
The PV Applications and Market Development Project provides an NREL focus to support the increasingly important analytical, applications, and market development efforts of the DOE Photovoltaics Program and the Office of Solar Energy Conversion. The overall objective of this project is to conduct a coordinated set of market conditioning and project development activities (through NREL in-house research, NREL subcontracted research, and technical support to DOE GO-contracted efforts) that lead toward sustainable U.S. and international markets for photovoltaic systems.

The project is divided into eight interrelated areas of activity, each led by an experienced NREL staff member, as shown in the table below. In many instances, the specific activities implemented within the PV Applications and Market Development Project cross both the activity and personnel boundaries implied below. This cross fertilization is encouraged by both PV Program and NREL line management and in every case leads to better activities and products. The delineations listed below are largely for administrative convenience and to identify a "lead contact."

### Project Activity Areas

<table>
<thead>
<tr>
<th>Activity</th>
<th>Activity Leader</th>
<th>Phone 303/384-6500</th>
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<tr>
<td>DOE-HQ staff support</td>
<td>Dave Mooney</td>
<td>202/586-1725</td>
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<tr>
<td>DOE-GO utility support (UPVG, PV4U, SCE, ....)</td>
<td>As needed</td>
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<tr>
<td>Solar 2000 Quarterly, India development</td>
<td>Jack Stone</td>
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<td>PV:BONUS Program Support, Sunrayce 95</td>
<td>Byron Stafford</td>
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<td>PV Education, Assistance and Training</td>
<td>John Thornton</td>
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<td>PV-DSM Analysis, China development</td>
<td>William Wallace</td>
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<tr>
<td>Sunrayce 93, Village Power Hybrid team, PV-DSM modeling, and Brazil support</td>
<td>Cecile Leboeuf</td>
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<tr>
<td>NREL PV Technology Transfer and Conferences</td>
<td>Robert McConnell</td>
<td>x6419</td>
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<tr>
<td>Brazil pilot project implementation</td>
<td>Roger Taylor</td>
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</table>

The accomplishments and ongoing efforts in each of these activity areas are briefly discussed in the following sections, which group the activities somewhat differently than the personnel groupings listed above.
DOE-GO utility support (UPVG, PV4U, SCE, ....)

The PV Applications and Market Development group provides extensive technical support to the Department of Energy's Golden Field Office. In addition to the PV:BONUS program described in a separate section below, the group provides proposal and ongoing project review for the U.S. electric utility-related cooperative agreements and grants administered by DOE-GO. During 1993, primary efforts went into critical review and evaluation of the UPVG/TEAM-UP/PV-COMPACT proposals. In addition, activities being initiated by Southern California Edison and Georgia Tech (for the '96 Olympics) are supported by the group.

International Market Development

Brazilian Rural Electrification Pilot Project

The United States Department of Energy, Office of Solar Electric Conversion, through NREL, is undertaking a cooperative joint pilot project with the Brazilian states of Ceará and Pernambuco through the state-operated utility companies Companhia Energetica de Ceara (COELCE) and Companhia Energetica de Pernambuco (CELPE), together with the Centro de Pesquisas de Energia Eletrica (CEPEL) in the Federal Republic of Brazil. The objective of the effort is to establish and assess the efficiency, operability, and reliability of solar energy based rural electrification.

This pilot consists of (a) providing photovoltaic (PV) electric lighting systems to 350 homes in the Sertao de Sao Francisco region in the Brazilian state of Pernambuco; and (b) providing PV electric lighting systems to about 400 homes and 14 schools in the outback of Ceará. Key systems and components such as photovoltaic panels, batteries, and charge controllers were provided by NREL to CEPEL in order to carry out Phase 1 of the project during 1993. NREL provided this equipment to Brazil through a subcontract with Siemens Solar Industries (SSI). The equipment was transferred to CEPEL under the terms of a separate, parallel contract between NREL and CEPEL for subsequent use by COELCE and CELPE. COELCE and CELPE are responsible for procuring the balance of system components not provided by NREL and performing the systems integration, installation, maintenance and evaluation. COELCE, CELPE, and CEPEL are jointly carrying out the implementation and evaluation of the cooperative rural electrification project in Brazil. CEPEL assists NREL, COELCE, and CELPE in the technical evaluation, installer training, results reporting, and overall project management.

In addition to this Phase 1 activity, commitments were initiated in 1993 that will result in expansion of the pilot project activities into 5 additional Brazilian states during 1994. A competitive Request for Proposal was released by NREL in December 1993 with the plan of expanding the number of Brazilian states involved as well as the applications diversity.

Activity Development in China

In late 1993 NREL began to develop contacts and arrange for a "scoping visit" to China in order to provide specific recommendations to DOE regarding project opportunities that DOE could initiate to further develop a U.S. presence in the Chinese PV market. In January 1994 a three person NREL team plus an industry representative visited China for 2 weeks meeting with government and provincial leaders.
Activity Development in India

In late 1993 NREL began to develop contacts and arrange for a "scoping visit" to India in response to a World Bank request for assistance in mobilizing the dispersement of a PV loan executed in 1993 between the Bank and India. In January 1994 a two person NREL team was dispatched to conduct the evaluation.

PV-Buildings Technology Development

During 1993 a major multi-year three-phase procurement was initiated that is directed at supporting the development of cost-effective PV products and product-supply/product-user relationships that provide a sustainable market for PV in the buildings sector. Titled PV:BONUS (Building Opportunities in the U.S. for Photovoltaics), the 5-year, $25M (DOE), government/industry cost-shared initiative is being contractually administered by DOE-GO as a financial assistance (cooperative agreement) program. Procurement and contract initiation should be completed during the 2nd quarter of FY93. This activity provides for continuing technical support to GO throughout the duration of this multi-year effort.

Four cooperative agreements were executed during 1993.

- Energy Conversion Devices (along with subtier organizations USSC, Ariz.PS, Bechtel, Detroit Edison, MERRA, Mich. PSC, Minoru Yamasaki Assoc., NAHB Research Center, Oakland CC, Solar Design Assoc.) began the development of alternative large area and shingle-like roofing systems based on the ECD/USSC amorphous silicon/stainless steel PV technology.
- Delmarva Power & Light (along with subtier organizations AstroPower, U. of Delaware, Ascension Technologies, AC Battery Corp) began the economic evaluation and product testing for a dispatchable PV system that may be marketed by DP&L to commercial electric utility customers.
- Solar Design Associates (along with subtier organizations Mobil Solar, now being transferred to Solarex with the departure of Mobil Solar from the PV business, and ...) is developing a high power (250-300 watt) ac PV module that will be totally self contained generating 120 V, 60Hz power. Such a module will be able to be paralleled together, be individually power tracked, and be able to be connected directly into a buildings' electric service entrance or other appropriate electrical interface.
- Fully Independent Residential Solar Technology (along with subtier organizations Bradley Builders, DKM, Solarex, PP&L, GMAC Mortgage, Johnson, Drexel, SMUD) is developing integrated PV energy systems for the modular home industry. These systems and homes will be marketed as stand-alone remote homes and as grid-connected units.

One additional PV:BONUS agreement with Advanced Photovoltaic Systems and several subtier organizations to develop a large-area PV window wall technology was still under negotiation between APS and DOE-GO as of this writing.

In addition to the direct support of GO for the PV:BONUS procurement, NREL has contracted with the American Institute of Architecture/Association of Collegiate Schools of Architecture, Joint Council on Architectural Research to conduct a project entitled: "Design for Photovoltaics:
Curriculum Development for North American Architecture School Faculty." The objective of the project is to begin to institutionalize PV-buildings concepts by developing guidance for architectural school faculty in North America on how to incorporate information on photovoltaics into the design curriculum. The materials developed over the course of this project are directly targeted at the 3,000 members and 32,000 students active in North American schools of architecture in any given year. During the fall of 1993 a trial run of the curricula developed was undertaken at four participating architectural schools (University of Oregon, Harvard University, Arizona State University, and the Technical University of Nova Scotia). In 1994 the curricula will be distributed to the 3,000 North American schools of architecture. The curriculum package consists of (1) the BOOKSHELF collection of five books, twelve reports and pamphlets, one magazine, two software programs, and two manufacturers' videos; the SLIDE SET consisting of nearly 500 slides of PV basics and applications; the DESIGN GUIDELINES to provide students with a quick way of approximately sizing PV arrays, assessing annual and daily electricity generation along with use profiles for various building types; and the QUESTIONS that are used to generate class discussion during solar energy seminars.

PV Assistance, Education and Training

The technical assistance, education and training activity provides for the continuation and enhancement of specific actions directed at accelerating the commercialization of currently cost-effective PV products, supporting utilities and other organizations investigating the possible purchase of a PV system to meet the electrical needs of a particular site, and developing and providing educational materials for student training.

In 1993 this activity involved several important technology assistance efforts, including the following:

Ron Lehr, a former commissioner in the Colorado Public Utilities Commission, continued to provide education assistance to state regulatory authorities and to support activities undertaken by the multiple stakeholder coalition known as PV for Utilities. Lehr has provided assistance to several state utility regulatory commissions and other interested parties, such as state energy officials and consumer advocates, in terms of information services and advice on establishing collaborative processes to address specific renewable energy issues, primarily associated with photovoltaics. Lehr is in the process of developing a more formal regulatory education activity and is a key advisor to state working groups formed through the PV for Utilities coalition.

Public Service Company of Colorado NREL set up two collaborative, cost-shared efforts with PSCo. In the 10,000 Trees Project, PSCo shared about 40% of total cost. In the second collaborative effort PSCo is purchasing several PV-powered streetlights that were loaned to NREL for testing as part of a larger effort to evaluate commercially available stand-alone PV lighting systems.

LaPlata Electric Association (LPEA) is a non-profit, customer-owned, rural electric cooperative based in Durango, Colorado, which serves southwestern Colorado and northern New Mexico. In 1992, LPEA was approached by a customer, the Lake TV Translator Association, Inc. Lake TV, which provides television service to about 2,500 people, needed to replace a 3,000 meter (10,000 foot) extension line that carried power from LPEA to the translator site. The translator is a small load of about 200 watts located on a mountain top. Of all the options investigated by LPEA, the only traditional approach that fully met the requirements of all parties including the
Forest Service, dictated a 5.6 kilometer (3.5 mile), 7,200 volt underground distribution system. In addition to an installation cost of nearly $325,000, annual operation and maintenance costs were expected to exceed $53,000 because of the rugged terrain. As an alternative, LPEA chose a PV system as the most cost-effective and reliable option. The installed cost of the recently completed 1.44 kilowatt (peak) PV system was $47,250, or about 15% of the estimated cost of the line extension. Annual maintenance costs are expected to be about $7,300. The lifetime of the PV system is expected to be comparable to the underground line.

At the Juniper Breaks Entrance Station for the Pueblo State Recreation Area near Pueblo, Colorado, approximately 111 kilowatt-hours per year of electricity was needed. The Colorado Office of Energy Conservation (OEC), which managed the project, obtained bids for conventional extension lines ranging from about $43,345 to $78,688. As an alternative, the OEC installed a 408 watt (peak) PV hybrid system with a backup propane-fired generator at the entrance station. The total installed cost, including backup generator, was about $15,841, or about 36% of the lowest cost line extension estimate.

Partial funding for both of these projects was provided by the National Photovoltaics Program at NREL. In return, NREL received detailed comparisons of PV vs. line extension costs for both projects. Summaries of these comparisons, along with similar data from several other PV projects, will be published by NREL in 1994 and will be made available to utilities and other interested parties.

Colorado Utility Renewable Energy Forum. As a result of an action item at the Tucson Conference in December 1991, NREL took the lead to set up and administer a Colorado State technology transfer group for renewables. Known as the Colorado Utility Renewable Energy Forum, the group now meets quarterly and has a consistent attendance of 60-80 engineers, regulators, state energy officials, utility executives, industry representatives and others. The group has become part of the PV4U state collaborative effort and is investigating possible projects activities.

Colorado PUC Activities. NREL continues to provide major written and verbal testimony to the Colorado PUC for continuation and revision of Rule 31. NREL also participated in the formulation of the Renewable Energy Docket and the establishment of the agenda for the several hearings.

1996 Atlanta Olympics. NREL continues to support the evaluation of a variety of PV projects that may be funded by DOE for the 1996 Olympic Games in Atlanta. Three types of PV opportunity areas exist. The first area includes the different venues: the equestrian, field hockey, shooting, tennis and swimming venues. The second area includes possible applications in the athlete housing area on the Georgia Tech campus. The third area includes urban revitalization or renewal projects instigated by MAOGA and others to take advantage of the unique opportunity offered by the Olympics. These areas lie in and around the Georgia Tech and the historic black colleges near downtown Atlanta.

In FY93 this activity also provided NREL support of the Soltech '93 conference, which was different from previous ones in that the conference used high-level, national known speakers for the plenary sessions, and was addressed to lawmakers, and other officials in Washington D.C.

In FY93 NREL developed and published a handbook on PV for Municipal Planners.
PV-DSM Analysis

NREL continues to lead the growing U.S. and international interest in PV as a demand-side management option. Coordination and management of two key subcontracts, along with many meetings and interactions with the Utility PV Group and others has established NREL leadership in this exciting new area. Coupled with the product development activities under PV:BONUS, PV as a DSM option is moving closer to reality.

The Center for Energy and Environmental Policy Research at the University of Delaware is conducting a project entitled: "Evaluation of DSM Opportunities for Photovoltaics." The objectives of this ongoing project are: 1) to evaluate existing residential, commercial and industrial DSM incentive programs with regard to incentive levels and utility avoided costs; 2) to analyze the interactions between incentive programs, avoided costs, and regulatory influences; 3) develop a spreadsheet evaluation model to describe the economic costs and benefits to electric utilities and their customers; and 4) to develop and promote the role PV can play in residential and commercial DSM programs. The first part of this work was completed in early 1993. The effort has now been expanded to focus on the development of the computer-based economic analysis tool (item 3) that captures both utility and customer benefits of PV-DSM. This computer tool is being validated with several participating utilities, and will be made available to UPVG and others upon completion.

The Atmospheric Sciences Research Center, State University of New York at Albany continued a project entitled: "Solar Resource/Utility Load Matching Assessment." The objectives of this study are to 1) investigate the viability of using insolation data measured by geostationary satellites to 2) infer the load matching capability of photovoltaic (PV) systems in selected electric utilities across the United States. By comparing PV load matching capability estimated from the satellite data with that obtained from ground measurements, it has been shown that satellite data can be used to provide a good indication of PV effective load carrying capability. During 1993 twenty participating utilities received a preliminary evaluation of PV's potential for contributing to meeting their system load requirements and are now better informed about how to pursue an interest in PV development. As with the DSM evaluation, the first part of this work was completed in early 1993. During 1994 additional utilities are being matched with their solar resource data - - an activity being conducted in cooperation with the UPVG.

NREL also supports the EPA residential and commercial demonstration program where two to six kW grid-connected PV systems are being installed in electric utility systems throughout the country. NREL will be evaluating the data collected from these systems for additional PV-DSM insights.

Sunrayce 93

Sunrayce is a DOE-sponsored biennial university design competition for solar-powered electric vehicles. It is dedicated to the educational development of university science and engineering students with its themes of Education, Energy, and the Environment.

The Sunrayce 93 activity provided for management and implementation of the 1055 mile, 7-day, 34 contestant, Dallas to Minneapolis race. The race was conducted June 20-26, 1993. Sunrayce provides a major educational forum for the engineering student participants and is an important forum for PV outreach to the general public as the race winds its way through the heartland of
University teams competed for the opportunity to participate in Sunrayce 93 via a competitive solicitation proposal process. The 36 successful teams had 1 year to design, build, and test the car prior to the cross country race, which traveled from Dallas to Minneapolis. The Sunrayce regulations required participation by each team in one of three qualifiers, where the cars were subjected to a rigorous inspection for safety and regulation compliance and a braking and handling test. Then, each car had to complete 50 miles at an average speed of at least 20mph on a closed track. Thirty-four teams passed the qualification test and participated in the race. All participating teams completed the race, and everyone arrived at the finish line safely.

NREL's role was to provide project management and technical and administrative support in all aspects of Sunrayce 93 execution. The NREL project team for Sunrayce drew participation from many divisions, including PV, Conferences, Editing, Graphics, Public Affairs, and the NREL Washington Office. Activities prior to the race event comprised staffing a hotline for students and interested public at Sunrayce HQ in Washington, the production and distribution of the award-winning monthly Sunrayce Dateline newsletter, and development of: Sunrayce brochures, a Sunrayce hands-on traveling exhibit, and media kits. All logistics, accommodations, local coordination in each town along the route, and all safety and communications activities were also managed at NREL. Public Relations efforts were coordinated by NREL in conjunction with DOE and GM.

NREL also developed and managed the external Sunrayce Organization, including function and responsibility definition for all advisory committee members, and task assignments which responded to direction from DOE HQ. Efforts of major corporate sponsors (such as GM and EDS), other government agencies (such as EPA), the Society of Automotive Engineers, and other laboratories (such as Sandia and Brookhaven) were coordinated. Additionally, NREL managed the solicitation, award, and performance of five technical support subcontracts for Sunrayce.

Sunrayce was featured on national network and local affiliate television, including CBS Morning News and CNN, representing NREL and DOE on Sunrayce 93. Participants and officials were also interviewed on numerous radio programs, including Voice of America. Hundreds of newspaper articles and several magazine articles covered the event.

The PV Applications and Market Development project has been assigned by DOE to manage the race again for 1995, Sunrayce 95. The competitive procurement for participating schools, and necessary internal management structuring for the 95 race has already been accomplished.

**NREL PV Technology Transfer**

The technology transfer and characterization task provides for continued documentation and support of NREL PV technology transfer activities (across all projects) and limited analysis of current PV technology status and systems issues, such as storage impacts and BOS cost trends. A new element in FY93 was the quarterly *NREL PV Program Technology Transfer Report* describing specific projects involving NREL and industry researchers. This report (1) provides guidance by example to NREL researchers interested in undertaking collaborative projects with U.S. industries, (2) documents the already extensive ongoing interactions, and (3) provides insights to U.S. Industries interested in involving NREL researchers in their internal projects. The report is circulated among the U.S. PV community.
In support of the need to increase communications regarding the Solar 2000 strategy, NREL produces *Solar 2000 Update*, a quarterly outreach document designed to be a resource for information on Solar 2000 activities. It includes technical status updates as well as the latest efforts in national and international manufacturing and market development.
## 8.0 List of Active Subcontracts

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<tr>
<th>Contractor, Principal Investigator, Address</th>
<th>Work Title (Research Activity)</th>
<th>Contract Number</th>
<th>FY 1993 Funding ($K)</th>
<th>Start/End Dates</th>
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<td><strong>CRYSTALLINE MATERIALS AND ADVANCED CONCEPTS PROJECT FY 1993</strong></td>
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<td>Colorado State University G. Collins Fort Collins, CO 80523</td>
<td>Arsine and Hydride Radical Generation for MOCVD Growth</td>
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<td>Georgia Instit. of Technology A. Rohatgi Atlanta, GA 30332</td>
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<td>Massachusetts Instit. of Technology L. Kimerling Cambridge, MA 02139</td>
<td>Role of Point Defects &amp; Impurities in Processing &amp; Performance of Crystalline Silicon Solar Cells</td>
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<td>N. Carolina St. Univ. G. Rozgonyi Raleigh, NC 27695</td>
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<td>New III-V Cell Design Approaches for Very High-Efficiency</td>
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<td>Spire Corp S. Vernon Bedford, MA 01730</td>
<td>Low-cost, High-efficiency Solar Cells Utilizing GaAs-on-Si Technology</td>
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<td>SUNY at Albany J. W. Corbett Albany, NY 12222</td>
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<td>Texas Tech. University Stefan Eistreicher Lubbock, TX 79409</td>
<td>Theoretical Analysis of Hydrogen-Vacancy Complex Formation &amp; Diffusion in Silicon</td>
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<td>Univ. of Calif. Berkeley E. Weber Los Angeles, CA 90089</td>
<td>Identification and Control of Lifetime Reducing Defects</td>
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<td>Univ. of Southern Calif. D. Dapkus Los Angeles, CA 90089</td>
<td>Atomic Layer Epitaxy for Low Temperature Growth of PV Materials</td>
<td>XM-0-19142-6</td>
<td>226.0</td>
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<td>Univ. of South Florida L. Jastrzebski Tampa, FL 33620</td>
<td>Optimization of Getting Processes for PV Silicon</td>
<td>XD-2-11004-5</td>
<td>110.0 (9 mos)</td>
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<td>University of Utah M. Delong Salt Lake City, UT 84112</td>
<td>Optical Processes in Ordered GaInP</td>
<td>XR-2-12121-1</td>
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<td>University of Illinois A. Rockett Champaign, IL 61820</td>
<td>Effects of Crystal Defects on CuInSe₂</td>
<td>XAD-3-12114-1</td>
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<td>University of Utah C. Taylor Salt Lake City, UT 84112</td>
<td>Electronic Processes in Thin-Film PV Materials</td>
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<td>Univ. of South Florida D. Morel Tampa, FL 33620</td>
<td>Heterojunctions in Thin-Film Solar Cells</td>
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<td>Johns Hopkins University Dr. Searson Baltimore, MD 21218</td>
<td>Solar Electric Conversion at Dye Sensitized Nanostructured Electrodes</td>
<td>XAD-3-12114-4</td>
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<td>North Carolina State Univ. S. Bedair Raleigh, NC 27695</td>
<td>High Efficiency Cascade Solar Cells</td>
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<td>SUNY at Buffalo W. Anderson Amherst, NY 14228</td>
<td>Thin Film Silicon by Constitutional Supercooling</td>
<td>XAI-3-11167-1</td>
<td>97.2</td>
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<td>Spire Corporation P. Maruska Bedford, MA 01730</td>
<td>High Performance (Porous) Silicon Solar Cells</td>
<td>XAI-3-11670-2</td>
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<td>Princeton University</td>
<td>Crystalline Organic Multiple Quantum-Well Solar Cells</td>
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<td>S. Forrest Princeton, NJ 08544</td>
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**POLYCRYSTALLINE THIN FILMS PROJECT FY 1993**

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<td>Astropower, Inc.</td>
<td>Monolithically Integrated Si-Film PV Modules</td>
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<td>J. Rand Newark, DE 19711</td>
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<td>Colorado State Univ.</td>
<td>Role of Polycrystallinity in CdTe &amp; CuInSe$_2$ PV</td>
<td>XC-0-10046-1</td>
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<td>J. Sites Fort Collins, CO 80523</td>
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<td>Colorado School of Mines</td>
<td>CdTe Solar Cells Fabricated by Electro-deposition</td>
<td>XG-2-11036-4</td>
<td>88.0 (7 mos)</td>
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<td>J. Trefny Golden, CO 80401</td>
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<td>Energy Photovoltaics (EPV)</td>
<td>Ultra-thin CIS Devices with Non-H$_2$Se</td>
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<td>A. Delahoy Monmouth Jct. NJ 08852</td>
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<td>Florida Solar Energy Ctr.</td>
<td>Polycrystalline CuInSe$_2$ &amp; CdTe PV Solar Cells</td>
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<td>N. Dhere Cape Canaveral, FL 32920</td>
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<td>Georgia Inst. of Tech.</td>
<td>Hi-Eff. CdTe Thin Film Cells</td>
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<td>A. Rohatgi Atlanta, GA 30332</td>
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<td>Golden Photon</td>
<td>High-Efficiency, Large-Area CdTe Panels</td>
<td>ZN-0-19019-1</td>
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<td>S. Albright Golden, CO 80401</td>
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<td>ISET</td>
<td>Novel Two-Stage Selenization Methods for Fabrication of Thin Film CIS Cells &amp; Sub-Modules</td>
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<td>V. Kapur Inglewood, CA 90301</td>
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<td>Purdue Univ.</td>
<td>Develop. and Applic. of Computer Model for CuInSe$_2$ &amp; CdTe Solar Cells</td>
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<td>R. Schwartz W. Lafayette, IN 47907</td>
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<td>Siemens Solar</td>
<td>Research on High Efficiency CuInSe$_2$ Based Modules</td>
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<td>Solar Cells Inc.</td>
<td>Fabrication of Stable Large Area Thin film CdTe PV Modules</td>
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<td>P. Meyers Toledo, OH 43615</td>
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<td><strong>Solarex</strong>&lt;br&gt;R. Arya&lt;br&gt;Newtown, PA 18940</td>
<td>Research on Poly-crystalline Thin Film Submodules Based on CuInSe₂ Materials</td>
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<td><strong>Univ. Colorado</strong>&lt;br&gt;A. Hermann&lt;br&gt;Boulder, CO 80309</td>
<td>Novel Thin Film CuInSe₂ Fabrication</td>
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<td><strong>Univ. of Delaware-IEC</strong>&lt;br&gt;R. Birkmire&lt;br&gt;Newark, DE 19716</td>
<td>Thin Film Materials and Devices</td>
<td>XAV-3-13170-1</td>
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<td><strong>Univ. of S. Florida</strong>&lt;br&gt;D. Morel&lt;br&gt;Tampa, FL 33620</td>
<td>Thin Film CdTe, ZnTe, &amp; Hg₁ₓZn₁₋ₓTe Solar Cells</td>
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<td>123.0 (8 mos)</td>
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<td><strong>University of Toledo</strong>&lt;br&gt;A. Campaan&lt;br&gt;Toledo, OH 43606</td>
<td>Thin Film CdTe Photovoltaic Cells</td>
<td>ZN-1-19019-3</td>
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<td><strong>Washington State Univ.</strong>&lt;br&gt;L. Olsen&lt;br&gt;Pulman, WA 99164</td>
<td>CuInSe₂ Solar Cells Based on ZnSe Windows</td>
<td>XG-2-11036-6</td>
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**AMORPHOUS SILICON RESEARCH PROJECT FY 1993**

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<td><strong>Advanced Photovoltaic Systems</strong>&lt;br&gt;F. Kampas&lt;br&gt;Princeton, NJ 08542</td>
<td>Stable Hi-Eff. a-Si Multijunction Modules</td>
<td>ZM-1-19033-2</td>
<td>500.0</td>
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<td><strong>Colo. School of Mines</strong>&lt;br&gt;D. Williamson&lt;br&gt;Golden, CO 80401</td>
<td>Small-Angle X-Ray Scattering Studies of Microvoids in a-Si-Based Semiconductors</td>
<td>XG-1-10063</td>
<td>46.0 (8.5 mos)</td>
<td>1/91-4/94</td>
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<td><strong>Harvard University</strong>&lt;br&gt;R. Gordon&lt;br&gt;Cambridge, MA 02138</td>
<td>Optimization of Transparent &amp; Reflecting Films for a-Si Solar Cells</td>
<td>XH-1-11032-1</td>
<td>132.0</td>
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<td><strong>Iowa State Univ.</strong>&lt;br&gt;V. Dalal&lt;br&gt;Ames, IA 50011</td>
<td>Comprehensive Research on Stability &amp; Electronic Properties of a-Si:H &amp; a-SiGe:H Alloys</td>
<td>XG-1-10063-8</td>
<td>264.0</td>
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<td><strong>National Institute of Standards &amp; Tech.</strong>&lt;br&gt;A. Gallagher&lt;br&gt;Boulder, CO 80303</td>
<td>Growth Mechanisms &amp; Characterization of a-Si:H Alloy Films</td>
<td>DD-1-11001-1</td>
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<td>North Carolina State Univ. G. Lucovsky Raleigh, NC 27695</td>
<td>Electrical &amp; Optical Properties of Microcrystalline Si &amp; a-Si,N:H Alloys</td>
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<td>Penn. St. Univ R. Collins Univ. Park, PA 16801</td>
<td>In-Situ Characterization of Growth &amp; Interfaces In a-Si:H Devices</td>
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<td>Solarex Corp. R. Arya Newtown, PA 18948</td>
<td>Stable Hi-Eff. a-Si Multijunction Modules</td>
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<td>Syracuse Univ E. Schiff Syracuse, NY 13244</td>
<td>Research on Defects &amp; Transport in a-Si Based Semiconductors</td>
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<td>Univ. of Delaware-IEC S. Hegedus Newark, DE 19716</td>
<td>Stable Hi-Eff. a-Si Based Solar Cells with Low Hydrogen Content</td>
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<td>Univ. of Delaware-IEC R. Birkmire Newark, DE 19716</td>
<td>Thin-Film Materials and Devices</td>
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<td>Univ. of Illinois J. Abelson/N. Maley Champaign, IL 61820</td>
<td>Research on Silicon-Carbon Alloys and Interfaces</td>
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<td>Univ. of North Carolina H. Daxing Chapel Hill, NC 27599</td>
<td>Recombination &amp; Metastability in a-Si &amp; Si Ge Alloys</td>
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<td>67.0 (8.5 mos)</td>
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<td>Univ. of Oregon J. Cohen Eugene, OR 97403</td>
<td>Microscopic Origins of Metastable Effects in a-Si:H &amp; Deep Defect Characterization in a-Si, Ge:H Alloys</td>
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<td>63.0 (8.5 mos)</td>
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<td>United Solar Systems Corp. S. Guha Troy, MI 48084</td>
<td>Hi-Eff. Multigap Multijunction a-Si Based Submodules</td>
<td>ZM-1-19033-2</td>
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<td>Xerox Corporation R. Street Palo Alto, CA 94304</td>
<td>Stability, Electronic &amp; Structural Properties of a-Si Silicon Alloys</td>
<td>XG-1-10063-9</td>
<td>208.0</td>
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PHOTOVOLTAIC MANUFACTURING TECHNOLOGY (PVMaT) PROJECT FY 1993

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<th>Start/End Dates</th>
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<td>Astro Power, Inc. S. Collins Newark, DE 19711</td>
<td>Silicon-Film™ Photovoltaic Manufacturing Technology</td>
<td>ZM-2-11040-5</td>
<td>1679.0</td>
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<td>Energy Conversion Devices, Inc. M. Izu Troy, MI 48084</td>
<td>Continuous Roll-to-Roll Amorphous Silicon Photovoltaic Manufacturing Technology</td>
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<td>ENTECH, Inc. M. O'Neill Dallas-Ft. Worth Airport TX 74261</td>
<td>PVMaT Improvements for ENTECH's Concentrator Module</td>
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<td>Mobil Solar Energy Corp. J. Kalejs Billerica, MA 01821-3980</td>
<td>Thin Edge-Defined Film-Fed Growth (EFG) Octagons</td>
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<td>Siemens Solar Industries T. Jester Camarillo, CA 93011</td>
<td>Photovoltaic Cz-Si Manufacturing Technology Improvements</td>
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<td>Solarex Corp. R. Oswald Newtown, PA 18940</td>
<td>Large Area Triple Junction a-Si Alloy Production Scale-up Project</td>
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<td>Automated Solar Cell Assembly Teamed Process Research</td>
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<td>Springborn Laboratories W. Holley Enfield, CT 06082</td>
<td>Teamed R&amp;D on Discoloration and Degradation of EVA</td>
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<td>Utility Power Group G. Duran Chatsworth, CA 91311 and Advanced Photovoltaics Systems (APS) H. Volltrauer Princeton, NJ 08542</td>
<td>Amorphous Silicon PV Manufacturing Technology Lower Tier Subcontract</td>
<td>ZM-1-11040-6</td>
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**PV MODULE AND SYSTEM PERFORMANCE AND ENGINEERING PROJECT FY 1993**

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<td>Bechtel J. Gough San Francisco, CA 94119</td>
<td>Photovoltaic Power Systems for the Solar Energy Research Facility</td>
<td>AAN-3-13306-01</td>
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<td>Energy Conversion Devices I. Masatsugu Troy, MI 48084</td>
<td>a-Si Utility/Industry Photovoltaic Power Project</td>
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<td>Energy Photovoltaics A. Delahoy Princeton NJ 08543</td>
<td>a-Si Utility/Industry Photovoltaic Power Project</td>
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<td>Integrated Power Corporation D. Panico Rockville, MD 20855</td>
<td>a-Si Utility/Industry Photovoltaic Power Project</td>
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<td>Solarex Corporation J. Morris Newtown, PA 18940</td>
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<td>SEIA R. Klein Washington, DC 20001</td>
<td>Mgmt. and Admin. of IEC/PV/TEC-83 Secretariat and Int'l Standards Development</td>
<td>HI-2-12006-9</td>
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<td>Solar Cells, Inc. J. Brown Toledo, OH 43615</td>
<td>1 kW CdTe PV System Technology Validation</td>
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<td>University of Colorado C. Bowman Boulder, CO 80303</td>
<td>PV Module Encapsulant Formulations</td>
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<td>United Solar Systems Corp. L. Slominski Troy, MI 48084</td>
<td>1.8 Kilowatt PV System of a-Si Dual Junction Modules</td>
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<th>Contractor, Principal Investigator, Address</th>
<th>Work Title (Research Activity)</th>
<th>Contract Number</th>
<th>FY 1993 Funding ($K)</th>
<th>Start/End Dates</th>
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<tr>
<td>Centro De Pesquisas De Energia Electrica (CEPEL) A. Mosse Rio De Janeiro Brazil 20001-970</td>
<td>Brazilian Rural Electrification Pilot Project</td>
<td>AAD-3-13179-01</td>
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<td>12/92 12/96</td>
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<td>R. Lehr, Consultant Denver, CO 80209</td>
<td>Regulatory Support for PV-DSM</td>
<td>CAT-3-13153-01</td>
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<td>SEIA S. Sklar Washington, DC 20001</td>
<td>Task Orders for Solar Journal PV4U Support PV Guidebook S. Awarbush Conferences</td>
<td>HI-2-12006-0 #55 #56 #56 #57 #58</td>
<td>35.0 99.0 80.0 135.0 45.0</td>
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<td>Siemens Solar Industries Camarillo, CA 93011</td>
<td>Brazil Rural Electrification Pilot Project</td>
<td>AAD-3-13181-01</td>
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<td>Univ. of Delaware J. Byrne Newark, DE 19616</td>
<td>Evaluation of DSM Incentive Opportunities for PV</td>
<td>XR-2-11248-1</td>
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<td>Southwest Technology Development Institute A. L. Rosenthal Las Cruces, NM 88003</td>
<td>Long-Term Environmental Effects on Roof-Mounted PV Modules</td>
<td>2-120014-1</td>
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This report summarizes the fiscal year (FY) 1993 (October 1, 1992, through September 30, 1993) progress of the subcontracted photovoltaic (PV) research and development (R&D) performed under the Photovoltaic Advanced Research and Development Project at the National Renewable Energy Laboratory (NREL). The mission of the national PV program is to develop PV technology for large-scale generation of economically competitive electric power in the United States. The technical sections of the report cover the main areas of the subcontract program: the Crystalline Materials and Advanced Concepts project, the Polycrystalline Thin Films project; the Amorphous Silicon Research project; the Photovoltaic Manufacturing Technology (PVMaT) project; the PV Module and System Performance and Engineering project; and the PV Analysis and Applications Development project. Technical summaries of each of the subcontracted programs provide a discussion of approaches, major accomplishments in FY 1993, and future research directions.