Polycrystalline Thin-Film Technology: Recent Progress in Photovoltaics

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On September 16, 1991, the Solar Energy Research Institute was designated a national laboratory, and its name was changed.
ABSTRACT

Polycrystalline thin films have made significant technical progress in the past year. Three of these materials that have been studied extensively for photovoltaic (PV) power applications are copper indium diselenide (CuInSe₂), cadmium telluride (CdTe), and thin-film polycrystalline silicon (x-Si) deposited on ceramic substrates.

The first of these materials, polycrystalline thin-film CuInSe₂, has made some rapid advances in terms of high efficiency and long-term reliability. For CuInSe₂ power modules, a world record has been reported on a 0.4-m² module with an aperture-area efficiency of 10.4% and a power output of 40.4 W. Additionally, outdoor reliability testing of CuInSe₂ modules, under both loaded and open-circuit conditions, has resulted in only minor changes in module performance after more than 1,000 days of continuous exposure to natural sunlight.

The field of polycrystalline thin-film CdTe module research has also resulted in several recent improvements. Module performance has been increased with device areas reaching nearly 900 cm². Deposition has been demonstrated by several different techniques, including electrodeposition, spraying, and screen printing. Outdoor reliability testing of CdTe modules was also carried out under both loaded and open-circuit conditions, with more than 600 days of continuous exposure to natural sunlight. These tests were also encouraging and indicated that the modules were stable within measurement error. The highest reported aperture-area module efficiency for CdTe modules is 10%; the semiconductor material was deposited by electrodeposition. Modules fabricated by screen printing have been reported with an efficiency more than 8% for an area of 1200 cm². A thin-film CdTe photovoltaic system with a power output of 54 W has been deployed in Saudi Arabia for water pumping.

INTRODUCTION

The Polycrystalline Thin-Film Program at the National Renewable Energy Laboratory (NREL), formerly the Solar Energy Research Institute, is part of the United States Department of Energy (DOE) National Photovoltaics Program. The objective of this program is to support research and development on cells and modules that meet DOE's long-term goals by achieving high efficiencies (15%-20%), low cost ($50/m²), and long-time reliability (30 years) [National Photovoltaics Five Year Research Plan, 1987].

During the last year, researchers in CuInSe₂, CdTe, and thin-film x-Si technologies have made significant progress toward achieving the DOE goals. This progress includes (i) the achievement of record thin-film power module (4 ft²) efficiencies of nearly 10% for CuInSe₂, (ii) a breakthrough CdTe cell efficiency of 13.4%, (iii) an accelerated growth of the U.S. industrial infrastructure supporting CuInSe₂, CdTe, and thin-film x-Si, and (iv) the continued success of multiyear outdoor stability testing on prototype CuInSe₂ and CdTe modules. Many of the technical goals include Siemens Solar Industries, Solarex Corporation, International Solar Electric Technology (ISE), Martin Marietta, and Boeing Aerospace and Electronics. Photon Energy and Solar Cells Inc. are involved in the CdTe research under this initiative. A program is also being addressed for the aggressive development of the thin silicon film on ceramic substrates by AstroPower. The major players in polycrystalline thin films outside of the United States are BP Solar in the United Kingdom, Matsushita Battery in Japan, and Microchemistry in Finland. All three of these groups are developing thin-film CdTe power modules. Additionally, as part of the Photovoltaics for Utility-Scale Applications (PVUSA) project, several emerging thin-film technologies are planned for field testing at Davis, California, during 1992. This paper will summarize the current status and technical results under the subcontracted research in the PVUSA program. In addition, the NREL-funded competition for university research subcontracts will be discussed.
(module efficiency, stability, and cost) associated with attaining truly low-cost PV (under 6 cents/kWh system cost) appear to be achievable by these technologies given existing research trends. Figure 1 shows the relative progress of the thin films toward high-efficiency, 1-ft² modules. With theoretical efficiencies of 23.5% for CulnSe₂ and 27.5% for CdTe, and ultimate practical efficiencies of 16%-18% [Sites, 1988], it is expected that similar progress will continue for these polycrystalline thin films. Correspondingly, module stability also appears to be excellent (see results below), with two Siemens Solar Industries CulnSe₂ modules measured at 99.8% and 97.5% of their original efficiencies after almost 1,000 days of outdoor testing at NREL.

U.S. PV INFRASTRUCTURE

Although NREL has maintained a small research program in CulnSe₂ and CdTe throughout the 1980s, the funding level was held at only about $3 million per year. This support was allocated to: (i) subcontracted activities in both CulnSe₂ and CdTe, (ii) internal Research and Development (R&D) in CulnSe₂, and (iii) various analysis and characterization support activities.

Technical achievements in the late 1980s, such as the 11% efficient, 1-ft² CulnSe₂ module [Mitchell et al., 1988] made by ARCO Solar (now Siemens Solar Industries), led to increased interest in polycrystalline thin films. One of the critical barriers to the progress of these technologies was the narrowness of their industrial base. At that time, the only industrial group making CulnSe₂ modules was ARCO Solar, and only a few other corporate entities were capable of making efficient CulnSe₂ cells (i.e., ISET and Boeing Aerospace). The state of the CdTe industry was very similar: Ametek had decided to end its participation in the CdTe film core program from which the RFP participants and NREL subcontractors listed in Table 1 are all working to develop successful prototype thin-film modules. Issues of module design

participants. This encouraged industrial participants to lead the R&D effort and encouraged collaboration and support between industry and the research efforts at universities. Total funding for the first year of the three-year awards was about $3 million. The objectives of the RFP were to (i) increase module areas and efficiencies toward the long-term DOE goal of 15%; (ii) increase cell efficiencies toward and beyond 15%; (iii) assist in the development of new, lower-cost processes, where appropriate; (iv) assure that all stability issues are addressed; (v) assist the development of a basic understanding of CulnSe₂ and CdTe materials and devices; and (vi) assure a U.S. leadership role in commercialization of CulnSe₂ and CdTe modules. Additionally, the stabilization and strengthening of the corporate infrastructure of these technologies was a major focus of the DOE/NREL increase in funding for polycrystalline thin films.

Those industrial "partners" who were awarded subcontracts under this RFP are listed in Table 1, along with the corresponding focus of their subcontracts. Listed in Table 2 are the ongoing participants in the NREL program, primarily universities. These organizations form a significant portion of the polycrystalline thin-film core program from which the RFP participants and NREL internal researchers have drawn support and collaboration. The subcontractors listed in Table 1 are all working to develop successful prototype thin-film modules. Issues of module design

| Table 1. Module Development Goals For Industrial Partners (November 1991) |
|-----------------|-------------------|------------------|
| **CulnSe₂**     |                   |                  |
| ISET            | Cu & In Sputtering/Selenization | 11% efficiency - 900 cm² |
| Siemens Solar   | Cu & In Sputtering/Selenization | 12.5% efficiency - 3900 cm² |
| Solarex         | Elemental Cu, In, & Se Sputtering | 12% efficiency - 900 cm² |

| **CdTe**        |                   |                  |
| Photon Energy   | Spraying           | 12.5% efficiency - 3900 cm² |
| Solar Cells Inc. | Close-Spaced Sublimation | 10% efficiency - 7200 cm² |

| **Silicon Films** |                   |                  |
| AstroPower       | Thin-Film x-Si on Ceramic Substrates | 12% efficiency - 1200 cm² |
and efficiency and prototype processes are the main focus. The annual NREL/DOE funding of these subcontracts is about $4.2 million, with another $1.9 million cost-shared contribution from the subcontractors. Thus, the total investment over the three-year initiative will be about $18 million. In addition to the subcontracts of Table 1, the Polycrystalline Thin-Film Program has one other industrial subcontract with Martin Marietta. The goals of this effort are to investigate deposition by a rotating cylindrical magnetron of copper and indium (the precursors for the selenization of CulnSe$_2$) and cadmium and tellurium (for CdTe), as well as some work in CdTe electrodeposition.

Until this fiscal year, the program was not able to address the infrastructural weakness of polycrystalline thin-film research at universities. However, an RFP for subcontracted research is now under way to support university research in both CdTe and CulnSe$_2$. It is expected that about 6 subcontracts will be awarded under this RFP with each subcontract funded at around $100K/year. In addition, the program has three ongoing university subcontracts (totaling about $740K) at Colorado State University and the Institute of Energy Conversion (IEC) at the University of Delaware, and the University of Toledo. The breakdown of funds in Fiscal Year (FY) 1992 for the Polycrystalline Thin-Film Program research will be about 75% for industry and 25% for universities. In addition, NREL funds an in-house research effort of about $3,300K annually.

### Table 2. Polycrystalline Thin-Film Program Support Participants  (November 1991)

<table>
<thead>
<tr>
<th>Organization</th>
<th>Topics</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Institute of Energy Conversion</td>
<td>Selenized &amp; Evaporated CulnSe$_2$ &amp; CdTe</td>
<td>Cells &amp; Device Modeling</td>
</tr>
<tr>
<td>University of Illinois</td>
<td>Sputtered/Evaporated CulnSe$_2$</td>
<td>Cells</td>
</tr>
<tr>
<td>University of Colorado</td>
<td>Rapid Thermal Processing of Cu/In/Se Films by Electroplating or Sputtering</td>
<td>Cells &amp; Materials Research</td>
</tr>
<tr>
<td>California Institute of Technology</td>
<td>Contact Investigation of CulnSe$_2$/Mo Interface</td>
<td>Device Modeling</td>
</tr>
<tr>
<td>National Renewable Energy Lab</td>
<td>Growth, Characterization, &amp; Fabrication of CulnSe$_2$ Cells</td>
<td>Cells &amp; Device Modeling</td>
</tr>
<tr>
<td>Colorado State University</td>
<td>Characterization &amp; Modeling of CdTe &amp; CulnSe$_2$ Cells</td>
<td>Device Modeling</td>
</tr>
<tr>
<td>Purdue University</td>
<td>Modeling of CulnSe$_2$ &amp; CdTe Cells</td>
<td>Device Modeling</td>
</tr>
<tr>
<td>University of South Florida</td>
<td>MOCVD &amp; CSS of CdTe &amp; ZnTe</td>
<td>Cells</td>
</tr>
<tr>
<td>Georgia Institute of Technology</td>
<td>MOCVD of CdTe &amp; Cd$_{1-x}$Zn$_x$Te</td>
<td>Cells</td>
</tr>
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</table>

COPPER INDIUM DISELENIDE

During the past decade, progress in CulnSe$_2$ technology has been significant. This PV material is now considered the leading thin-film candidate in terms of efficiency and long-term reliability [Zweibel and Ullal, 1989]. Theoretical efficiencies for CulnSe$_2$ have been reported as high as 23.5% [Sites, 1988], resulting in this material being viewed as having significant potential as a low-cost, thin-film PV material.

Several deposition processes have been used in its fabrication (coevaporation, electrodeposition/selenization, spraying, screening printing, close-spaced vapor transport, hybrid evaporation/sputtering, electron-beam-evaporation/selenization, sputtering/selenization, reactive sputtering, sputtering/laser-assisted annealing, sputtering/rapid thermal processing, and metal organic chemical vapor deposition [MOCVD]) [Zweibel et al., 1990]. These options range from the experimental to those that have been proven at the prototype manufacturing level.

**CulnSe$_2$ Power Module - Siemens Solar Industries**

Of the numerous advances in the last year, perhaps the most significant was the achievement of a near-10%, encapsulated, CulnSe$_2$ power module by Siemens Solar Industries. Because thin-film modules come in many sizes, it is somewhat difficult to develop perspective about the relative importance of their efficiencies and areas. However, in overall technical progress, it is probable that the Siemens Solar CulnSe$_2$ power module is the most significant achievement in thin-film PV. No other module of this size has even come close in efficiency. Figure 2 shows the NREL-measured I-V curve of this module with an aperture-area (3883 cm$^2$) efficiency of 9.7%, $P_{max} = 37.7$ W; $V_{mp} = 24$ V; $J_{sc} = 2.44$ A; and FF = 64.4%.

**Improved CulnSe$_2$/Mo Adhesion - ISET**

ISET has been successful in fabricating CulnSe$_2$ cells by selenization of Cu/In precursor films with a total-area efficiency of 11.5%. Analysis by Sites (1991) has suggested that the junction properties of ISET CulnSe$_2$ cells (in terms of diode quality factors and recombination currents) are as good or better than those of any other CulnSe$_2$ devices available. Their properties are comparable to those needed for CulnSe$_2$ cells to achieve a 15% efficiency. Like other organizations involved in CulnSe$_2$ fabrication, especially those that use selenization, ISET has encountered adhesion problems at its CulnSe$_2$/Mo interface. In July 1991, ISET was granted a U.S. Patent [Basol and Kapur, 1990] on an innovative solution to the adhesion problem: the deposition of a very thin tellurium layer (10-500 Å) between the Mo and the CulnSe$_2$. ISET has claimed in its patent that this layer reduces adhesion problems significantly and also results in a device with improved performance. By adding the Te layer, ISET has been able to increase the flexibility with which it adds subsequent Cu and In (and Ga, if desired) layers. For example, ISET researchers prefer to deposit In and then Cu, the reverse of the conventional order.
Several record CdTe cell efficiencies were reported during the last few years. Based on a band gap of 1.45 eV, which is an optimum match with the solar spectrum, this material has theoretical efficiencies as high as 27.5% [Sites, 1988]. Given this significant potential, it is reasonable to expect that CdTe devices may achieve practical efficiencies of 18%.

Several methods are used for depositing CdTe thin films (electrodeposition, spraying, screening printing, close-spaced vapor transport, chemical vapor deposition, hot-wall evaporation, ion-assisted evaporation, laser-assisted evaporation, thermal evaporation, sputtering, sputtering/laser-assisted annealing, molecular beam epitaxy, and MOCVD). At this time, the most promising low-cost approaches are electrodeposition and spraying. Screening printing, a low-cost process, has had limited success due to its limitations in module processing.

Although intrinsic device stability appears good with all polycrystalline thin films, there are issues at the module level that need to be addressed. Several record CdTe cell efficiencies were reported during the last year [Sites, 1991]. In some cases, however, these reports were not validated by independent measurements. In specific cases, for instance, questions concerning excessive current densities suggest that the reported efficiencies were inaccurate. On the other hand, NREL did measure cells from Photon Energy and then from T.L. Chu (a lower-tier subcontractor of Photon Energy at the University of South Florida) that surpassed previously verified results.

In May 1991, Photon Energy produced a small-area (0.3 cm²) cell with exceptionally high current density (26.2 mA/cm²). This current density, which is about 90% of the theoretical maximum for CdTe, was achieved by using an optically thin CdS layer. This glass/ITO/CdS/CdTe cell had a quantum efficiency of 80% at the 400-nm wavelength (Figure 3), a strong indication that much of the improved current was coming from a reduction in the absorption of photons with energies above the CdS band gap.

Three weeks later, Chu substantially surpassed the Photon Energy result. Chu achieved a 13.4%-efficient CdS/CdTe cell with an area of 1.2 cm², Voc = 840 mV, and FF = 72.6%. This was reached by again achieving very high voltages and fill factors (shown in Figure 4). Another Chu cell having a 12.6% efficiency demonstrated the highest known CdTe fill factor to date, 74.6%.

These results were achieved using an innovative deposition process for the solution growth of CdS with both Chu’s own CdTe (made by close-spaced sublimation) and with Photon Energy’s CdTe materials (demonstrating up to 890 mV). The consistency of these high voltages suggests that much of the improved efficiency can be attributed to the solution-grown CdS rather than to the CdTe.

However, there is still room for improvement in these cells because the current densities of the Chu devices were moderate - about 20-22 mA/cm². The nature of the results of this CdS layer research suggests that further progress on these devices will be relatively easy, especially because the solution-grown CdS layer is not yet optimized for optical thinness. It is expected that this optimization and the achievement of cell efficiencies over 15% will be a focus in upcoming months.

OUTDOOR TESTS AND STABILITY ISSUES

Technical progress in CdTe research has also been significant in the past few years. Based on a band gap of 1.45 eV, which is an optimum match with the solar spectrum, this material has theoretical efficiencies as high as 27.5% [Sites, 1988]. Given this significant potential, it is reasonable to expect that CdTe devices may achieve practical efficiencies of 18%.

Several methods are used for depositing CdTe thin films (electrodeposition, spraying, screening printing, close-spaced vapor transport, chemical vapor deposition, hot-wall evaporation, ion-assisted evaporation, laser-assisted evaporation, thermal evaporation, sputtering, sputtering/laser-assisted annealing, molecular beam epitaxy, and MOCVD). At this time, the most promising low-cost approaches are electrodeposition and spraying. Screening printing, a low-cost process, has had limited success due to its limitations in module processing.
require attention as these technologies move into the marketplace. For instance, CuInSe₂ and CdTe are sensitive to chemicals used in module fabrication. Therefore, various approaches need to be developed for minimizing chemical interactions. Additionally, CdTe cells and modules are sensitive to water vapor, requiring careful encapsulation. Issues with CuInSe₂ modules tend to be associated with specific layers, such as undesirable MoSe layers at the back contact that impede current flow, and defects and adhesion issues associated with Mo and CuInSe₂ interfaces. Therefore, the achievement of a 30-year life for these technologies appears to require attention to specific processing details and careful module design and encapsulation.

To this date, the results of almost three years of outdoor tests on Siemens Solar Industries CuInSe₂ modules are very promising. NREL has conducted these tests on only two of these CuInSe₂ modules; however, the most recent measurements indicate that both of these modules are producing power at 99.8% and 97.5% of their original levels (Figure 5). The aperture-area efficiencies of the modules were near 8% with measurements taken at near-standard conditions. This accounts for some of the scatter in the data. Those data appear to indicate that the intrinsic stability of these modules is not an issue for CuInSe₂. Any remaining stability issues associated with this material are expected to be process- and design-specific.

The outdoor test results for Photon Energy CdTe modules are also promising; however, some issues remain. As can be seen from Figure 6 (outdoor tests, near standard conditions), several Photon Energy modules have shown good outdoor stability over reasonably long periods. However, other modules (not shown) have exhibited some slight degradation. Photon Energy believes that the deficiency in these modules is associated with encapsulation and edge-sealing techniques. Photon Energy modules are expected to improve as encapsulation issues are dealt with successfully.
"Product III" technology. Product II essentially uses a metallurgical barrier deposited on a low-cost conducting ceramic substrate. This barrier also serves as an optical reflector to enhance the short-circuit current and improve the cell efficiency. In addition, the thickness of the Si-film in Product II will be reduced to less than 50 microns. Product III incorporates a monolithically integrated 1,200-cm² module fabricated on an insulating ceramic substrate.

IEC has fabricated 10%-efficient small-area CuInSe₂ devices by the selenization method using H₂Se. IEC was also successful in fabricating 7%-efficient small-area devices by depositing Cu, In, and Se layers and heat-treating them in an atmosphere of excess Se. IEC also carried out modeling studies in support of both the CuInSe₂ and CdTe research. From this effort IEC has concluded that (i) the V_{oc} of CuInSe₂ solar cells cannot be solely described by a Shockley-Read-Hall (SRH) recombination mechanism, (ii) CdTe solar cells operate as p-n heterojunctions with their current dominated by SRH recombination in the junction region, and (iii) ZnTe:Cu contacts in an n-i-p CdTe structure are more stable than either Au or Cu-Au contacts.

The NREL in-house emphasis over the last year has been on the understanding of the phase behavior and microstructure of Cu/In precursors used in selenization processes for CuInS₂. In these processes, the fabrication of a precursor structure (containing mainly Cu and In deposited onto Mo-coated substrates) precedes the actual selenization step. A correlation of the Cu/In precursor microstructure with the post-selenized CuInS₂ film and device characteristics should identify techniques for enhancing the quality of CuInS₂ films for optimum device efficiency. Additional research has also been carried out on the compositional and substrate temperature dependencies of co-evaporated CuInS₂ films. The goal of this work is to optimize the fabrication process by deliberate modification and better control to achieve higher-quality CuInS₂ films.

TRANSITION TO MANUFACTURING

Three of the participants in the NREL Polycrystalline Thin-Films Project (Siemens Solar Industries, Photon Energy, and AstroPower) were winners in the most recent (1990) PVUSA Emerging Technology competitions. However, the developmental work that exists between the achievement of an excellent prototype module and an actual manufactured module is significant. The three technologies in question (CuInSe₂, CdTe, and thin-film x-Si) have reached an excellent level of laboratory success; however, the transition to true production has only recently begun. NREL is supporting these technologies during this transition, and we recognize that delays and unexpected problems are natural. This delay in the maturing of the technology has resulted in a postponement in delivery of the 20-kW systems required from both of these organizations under this program.

The problems associated with the final maturity of polycrystalline thin-film module products require that specific problems be addressed by each manufacturer. These include (i) identifying all process steps for cost-effective module production, (ii) completing the design of successful encapsulation schemes, (iii) confirming module reliability with outdoor and accelerated tests, and (iv) developing a market acceptance for these untried polycrystalline modules. In addition, each organization will have to fully address environment, safety, and health (ES&H) issues such as plant safety, plant waste disposal, and related matters. In parallel, the technologies must still progress toward higher efficiencies (10%-15% modules) if they are to make the kind of impact on global energy production that the DOE/NREL program believes is possible.

CONCLUSIONS

Polycrystalline thin-film CuInSe₂ and CdTe cell and module products have made rapid advances and are now recognized, in terms of efficiency and stability, as the leading thin film and photovoltaics. They have attained the highest cell efficiencies (14.1% for CuInSe₂ and 13.4% for CdTe), the highest module efficiencies (11.1%-CuInSe₂ on 1 ft²; 9.7%-CuInSe₂, 4 ft²); the best stabilities (CuInSe₂ - three years without degradation, CdTe - two years without degradation), and are made by the lowest-cost processes (spraying, electrodeposition, sputtering, and selenization). Both CuInSe₂ and CdTe are now moving out of the lab and into module demonstrations in the form of PVUSA projects, and we can be optimistic about both of them achieving the DOE long-term goal of 15% efficiency for their modules. However, the strengths of the polycrystalline thin-film materials remain somewhat obscure because progress in the laboratory and at the prototype module level still needs to be translated into success with manufactured products. In order to achieve a production yield for 10%-15% efficient modules, further required research should be focused on identifying all required process steps, successful encapsulation methods, market acceptance schemes, and all ES&H issues.

ACKNOWLEDGMENT

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