SERI/TP-211-2339
UC Category: 63
DE84004526

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May 1984

Presented at the
17th IEEE PV Specialists Conference
Orlando, Florida
1-5 May 1984

Prepared under Task No. 3432.10
FTP No. 462

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
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Prepared for the
U.S. Department of Energy
Contract No. DE-AC02-83CH10093

Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price:
Microfiche A01
Printed Copy A02

ADVANCES AND OPPORTUNITIES IN THE AMORPHOUS SILICON RESEARCH FIELD

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ABSTRACT

The amorphous materials and thin-film solar cells program was initiated by the U.S. Department of Energy in 1978 and then transferred to the Solar Energy Research Institute. The aim of the present DOE/SERI program is to achieve 5-year DOE research goals by addressing photovoltaic research in single-junction amorphous thin films as well as the most promising option in high-efficiency, multijunction solar cells. Multiyear subcontract awards initiated in 1983 were designed to demonstrate a stable, small-area, p-i-n solar cell of at least 12% (AM1) efficiency, a stable submodule of at least 8% (AM1) efficiency (total area, 1000 cm^2), and a proof-of-concept multijunction amorphous silicon alloy thin-film solar cell that will lead to achieving an 18% efficiency goal in 1988.

INTRODUCTION

Progress in the research, development, and commercialization of amorphous silicon for solar cells has surprised even its strongest proponents. Since 1974, when the first amorphous silicon solar cell was made, the 10% conversion efficiency milestone has been reached by one team (1) in 1982; now, seven research teams have reported conversion efficiencies of 10% and higher. Solar batteries using amorphous silicon solar cells for consumer products were first introduced in 1980 and are now being produced at a rate of 7 million units per month. The consumer market accounted for about 3 MW_p of amorphous silicon photovoltaic (PV) devices, 15% of all PV cells marketed in 1983 (2).

Research into the properties of amorphous silicon began in laboratories in the United States and abroad from 1968 to 1974. Scientists demonstrated experimentally that, contrary to general opinion, amorphous materials, particularly hydrogenated amorphous silicon, can be grown that have the optoelectronic properties necessary for use in thin-film solar cells. The first hydrogenated amorphous silicon PV cell was produced in 1974 by RCA scientists, and was the subject of a 1977 U.S. Patent (3). In July 1976, the U.S. Government issued a subcontract to RCA to support the research and development of amorphous silicon for applications in photovoltaics. On November 4, 1978, the U.S. Congress passed the Solar Photovoltaic Energy Research, Development, and Demonstration Act. This action, as well as those of the Japanese Government, significantly influenced research and development in solar energy by providing substantial increases in funding.

In July 1982, not too many years after the first PV cell was made, RCA announced the first demonstration of an amorphous silicon solar cell having a conversion efficiency of 10% (1), the efficiency figure established by government and industry experts as a crucial goal if thin-film solar cells were to be viable for large-scale electric power generation applications. Of the seven research teams that have reported conversion efficiencies of at least 10%, Komatsu (4) of Japan has announced the highest to date: 10.7%.

Based on continuing improvements in photovoltaic conversion efficiency and scientific understanding during the past decade, the U.S. Department of Energy (DOE) considers amorphous silicon cell technology to be a strong contender for photovoltaic power systems that will be capable of competing economically with conventionally produced electric power in the 1990s and beyond. To meet the technological requirements for PV electric power applications, DOE, through the Solar Energy Research Institute (SERI), developed a multiyear program plan based on government/industry partnerships. These government/industry cost-shared programs are supported by a core government-sponsored research program that consists of researchers at universities, at DOE Research Centers (SERI, JPL), at other government laboratories, and also by scientists in the private sector. Objectives of the plan are to expand the state of the art in single-junction amorphous silicon solar cells to achieve higher conversion efficiencies over larger areas and to expand the data base on amorphous silicon alloy materials for use in potentially higher efficiency, multijunction solar cells. The plan represents a balanced, phased approach by addressing PV research in single-junction amorphous thin films as well as the most promising options in high-efficiency, multijunction solar cells. Although the degree of uncertainty associated with options in these multijunction concepts remains high, the multiple approach of single-junction thin films and multijunction concepts makes the probability of total program success very high.

RESEARCH PROGRAM

The current Research and Development Subcontracts Program includes 16 subcontractors: seven with industry, seven with universities, and two government laboratories. Researchers at the DOE Research Centers (SERI and JPL) are also involved in amorphous silicon research. The program is divided into two primary and five supporting research activities. The two primary research activities are single-junction solar cells and multijunction, stacked solar cells. The supporting research activities encompass material deposition rate, alternative material deposition methods, light-induced effects, device testing and reliability, and theory. The two primary research activities involve strong government/industry partnerships using multidisciplinary teams whose objective is to improve PV device efficiencies. The requirements for such multidisciplinary research are based on the fact that various parts of thin-film PV devices are strongly interdependent and cannot be easily isolated. This is a consequence of the thin-film nature of the technology whereby surfaces/interfaces play a major role in the properties of the device. Research in single-junction solar cells will lead to meeting the near-term DOE goals on thin-film PV modules and will also provide the basis for the longer-term development of multijunction, stacked solar cells. Multijunction, stacked solar cells have the potential to meet higher efficiency goals. Secondary research support activities relate to specific tasks that support the two primary activities and, in addition, provide the mechanism to investigate newer options.

Figure 1 shows budget allocations for current subcontracted programs. The principal materials being examined are hydrogenated amorphous silicon, amorphous silicon-carbon and silicon-germanium alloys, microcrystalline phosphorus-silicon-hydrogen, microcrystalline boron-silicon-hydrogen, and passivators for reducing defects. Device structure is limited to p-i-n; other structures are used for diagnostic purposes. Thin-film preparation approaches are currently restricted to glow discharge (dc and ac) deposition in the two primary research activities. Glow discharge deposition using higher order silane gas is also being investigated for high growth rates. Chemical vapor deposition (CVD) using higher order silane gases for film preparation is the only other preparation method currently supported. The optoelectronic properties of amorphous materials are being studied by all methods, with an emphasis on minority carrier diffusion length.

EFFICIENCY STATUS

The historical trend of the efficiency of p-i-n solar cells for small and large areas is shown in Figure 2. The most rapid progress in cell efficiency has occurred since 1978. For small-area (~1 cm^2) solar cells, the cell efficiency was 4% in 1978, reached 10.1% in July 1982, and is presently reported to be at 10.7%. These achievements were for so-called p-i-n type solar cell structures with the amorphous material grown by glow discharge deposition. For larger area solar cells, the p-i-n cell efficiency was 2% in 1979 for an area of 50 cm^2, and it is now over 5% for a total area of 350 cm^2. U.S. companies not under government contract have reported conversion efficiencies over 8% for an area of 100 cm^2.

Table 1 gives performance data on the best reported single-junction p-i-n amorphous silicon solar cells having an area of at least 1 cm^2. The cell structure used by all four groups is the same (5,6,7). Four other research groups [Komatsu, Kyocera (8), Sanyo (9), Taiyo-Yuden/ETL (10)] have reported efficiencies above 10%, but over smaller areas. The highest reported efficiency is 10.7%, given by Komatsu for an area of 0.032 cm^2. In Table 2, the best individual PV parameters achieved in different

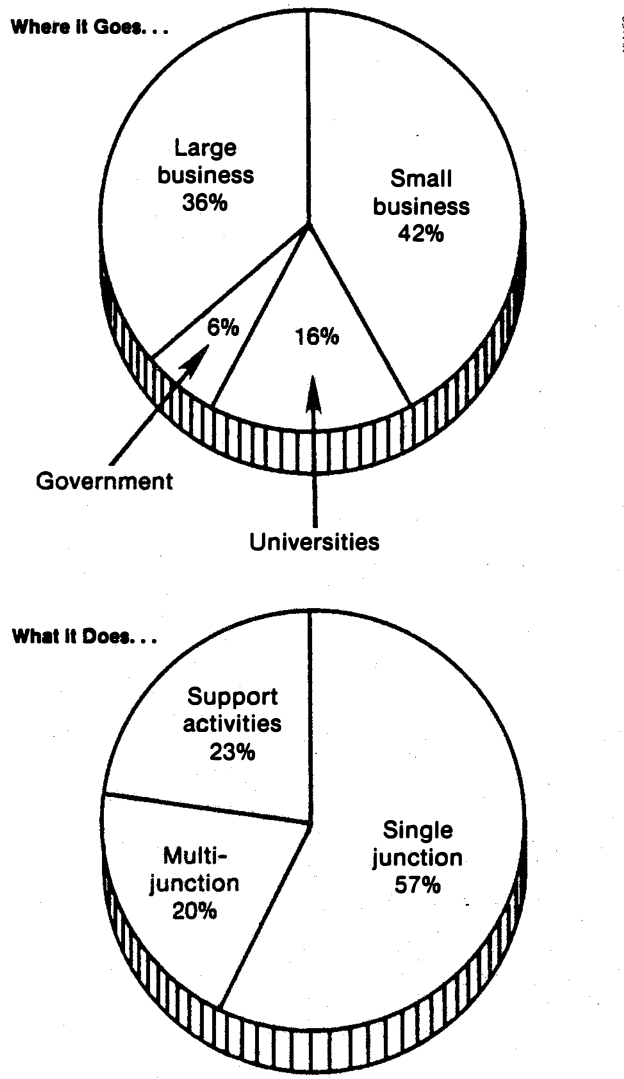


Figure 1. Budget Allocations for the Amorphous Materials Subcontracted Program, Fiscal Year 1984 (October 1, 1983 - September 30, 1984)

years along with calculated efficiencies using these parameters and a range of actual experimental efficiency values achieved in that year are reported. These data have been one of the better barometers for predicting future trends. The calculated efficiency obtained in this manner was 6.7% in 1979 and is now over 14%—a doubling in efficiency. This can be compared with actual experimental values of 4.5% in 1979 and 10.7% in 1984—again, a doubling in efficiency. The short-circuit current density (J_{SC}) remained near 14 mA/cm^2 for 1979, 1980, and 1981.

The increase in J_{SC} that occurred from 1981 to 1982 was caused by two developments. The first was the successful use of a new p-type material (boron-doped hydrogenated amorphous silicon carbide) which increased the collection efficiency in the optical wavelength region of less than 0.6 μm. The p-type material previously used (boron-doped hydrogenated amorphous silicon) absorbed

Structure	V_{oc} mV	J_{sc} mA/cm²	FF %	Eff. %	Area cm²	
Glass/TCO/p(a-SiC:H)-i-n(a-Si:H)/Me	830	18.3	68.9	10.5	1.05	Tokyo Denki Kagaku
Glass/TCO/p(a-SiC:H)-i-n(a-Si:H)/Me	840	17.8	67.6	10.1	1.09	RCA
Glass/TCO/p(a-SiC:H)-i-n(a-Si:H)/Me	850	16.1	71.0	9.7	4 cm²	ARCO Solar
Glass/TCO/p(a-SiC:H)-i-n(a-Si:H)/Me	870	15.5	68.4	9.2	1.0	FUJI

Table 1. Performance of Best Reported Single-Junction p-i-n Amorphous Silicon Solar Cells at least 1 cm² in Area

Best Parameters V_{oc} mV	J_{sc} mA/cm²	FF %	Calculated Efficiency %	Year	Experimental Efficiency %
990	18.8	76	(14.1)	1984	10.0 - 10.7
950	16.7	74	(11.7)	1982	7.5 - 10.1
910	14.0	70	(8.9)	1981	6.6 - 7.5
900	14.0	66	(8.3)	1980	5.0 - 6.6
800	14.0	60	(6.7)	1979	4.0 - 5.0

Table 2. Best Individual Parameters of Single-Junction p-i-n Amorphous Silicon Solar Cells

some of the incoming light without contributing to the conversion efficiency. The second development was the integration into the cell structure of a highly optically reflecting back-surface electrode such as an n-type microcrystalline/silver back contact. This highly reflective back contact permitted more optical absorption because of the increased path length of the longer wavelength photons.

Two research advances were responsible for the increase in J_{sc} from 1982 to 1984. The first was the successful integration in the cell structure of a thin, texturized surface layer between the transparent conductor and the amorphous silicon. The texturized layer provides better utilization of incoming light by reducing reflection and lengthening optical paths in the amorphous silicon material. The second advancement was a major step in the development of this technology toward commercialization. Researchers demonstrated that a thick, intrinsic amorphous silicon layer of at least 1 μm, rather than the conventional thickness of 0.6 μm, improved cell efficiency. So, the present material has better photovoltaic properties than the material previously used. In addition, the successful use of the thicker intrinsic amorphous silicon layer negates the need for a highly reflecting back contact. As experimental values of current density have recently reached as high as 19 mA/cm^2 (very close to theoretical values of 20-22 mA/cm^2 for an optical bandgap of 1.7 eV), there is little room for further increases in short-circuit current density.

Improvements in the conversion efficiencies of solar cells reflect intrinsic amorphous silicon material with better transport properties. Figure 3 shows that the electron drift mobility was 10^{-1}-10^{-2} cm^2/V-s in 1970 and is now 2.5 cm^2/V-s. The hole diffusion length was 0.02-0.2 μm in 1980 and is now near 1.8 μm. Also, the early consensus of device modelers of the hole collection in solar cells using amorphous silicon was that holes were collected only from regions of high electric field. The main reason for the significant improvement in transport properties and solar cell performance remains unanswered. There is no doubt that the level of impurities has been reduced and that this accounts for some improvement. However, it is more plausible that the major influence on material properties is changes in the microscopic structure. In other words, the present material is structurally different from the material of an earlier era.

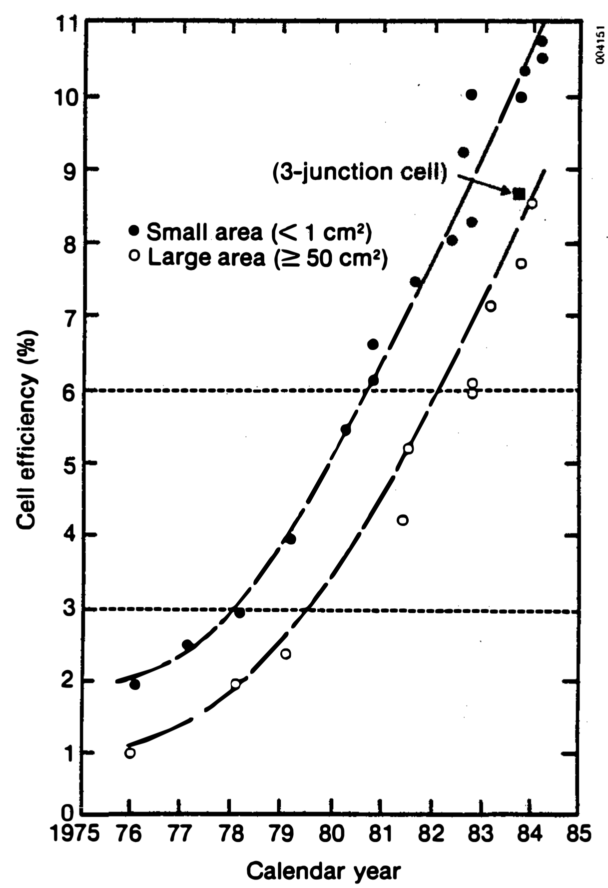


Figure 2. a-Si p-i-n Solar Cells prepared by Glow Discharge

- Electron drift mobility (μ_n) cm^2/v-s at 300° K
- – 1983: 2.5 R. Street
- – 1980: 10^{-1} - 10^{-2} R. Crandall
- – 1970: 10^{-1} - 10^{-2} P. LeComber, W. Spear
- Hole drift mobility (μ_H) cm^2/v-s at 300° K
- – 1983: 10^{-2} - 3 × 10^{-3} depends on field R. Street
- Hole diffusion length (Lp) μm
- – 1983: 1.3 - 1.8 Dresner, Moore, Goldstein, Szostak
- – 1977 - 1980: 0.03 - 0.2 Staebler, Crandall, Wronski

Consensus at earlier time was that hole collection is restricted to high-field depletion region and rest of cell remains inactive.

Figure 3. Transport Properties of Undoped Amorphous Silicon

NEW MULTIYEAR PROGRAMS

The U.S. Amorphous Silicon Research Plan calls for advancing the state of the art by way of multiyear subcontracts based on strong government/industry partnerships. Implementation of the plan began early in 1983 when multiyear, competitive procurements were issued in single-junction cells/submodules and multijunction cells. The procurement was weighted toward the nearer-term single-junction solar cell technology. The objective of the single-junction initiative is to improve the understanding and the efficiency of cells/submodules using single-junction p-i-n type cells based on material grown by the glow discharge deposition method. The objective of the multijunction initiative is to perform research on amorphous silicon alloy materials; in the structure of stacked cells, research is directed to establishing a base of knowledge that will help achieve efficiencies greater than 20% in the long term.

The competitive procurement process was completed on February 1, 1984, when the final subcontract was signed. Subcontracts were awarded to four research teams: Chronar Corporation, 3M Corporation, Solarex Corporation, and Spire Corporation. Figure 4 shows the different technical approaches taken by each company to achieve the program goals. Amorphous silicon material for single-junction solar cells will be deposited using three-chamber reactors, and material for multijunction solar cells will be deposited using six-chamber reactors. DC or RF glow discharge with two or three electrodes will be used to generate the plasma.

The total program cost over the three-year life of the subcontracts is $18.6 million, with approximately 70% of the total cost contributed by the government and about 30% contributed by the industrial subcontractors. Some subcontractors are developing a multichamber deposition system to fabricate the solar cells entirely on company funds, so the cost of this work is not included in these values. Goals of the program are to demonstrate stable p-i-n solar cells of at least 12% (AM1) efficiency with areas of at least 1 cm^2, a stable submodule of at least 8% (AM1) efficiency having a total area of at least 1000 cm^2, and proof-of-concept multijunction amorphous silicon alloy thin-film solar cells that will lead to achieving an 18% efficiency goal in 1988.

The enhanced U.S. government program plays a major leadership role in continuing the technological development of thin-film amorphous solar cells. Companies such as 3M Corporation have now joined with the government to develop single-junction solar cells, and the Polaroid Corporation is providing Spire Corporation with additional resources in its research into multijunction amorphous silicon alloy solar cells. The significant amorphous silicon technology developed at RCA, under long-term government and RCA support, is being successfully transferred to Solarex, one of the teams under subcontract to DOE/SERI to continue the development of single-junction solar cells. In addition, two small businesses—Chronar Corp. and Spire Corp.—are included in this government/industrial effort. Small businesses in the U.S. historically have been leaders in developing new technologies. Researchers at universities and DOE Research Centers support the government/industrial initiative by performing long-term basic research studies, by investigating problems requiring skills and equipment not readily available at many industrial laboratories, by assisting subcontractors in the solution of problems, and by maintaining a data base for technology transfer.

OTHER PROGRAM ACTIVITIES

In addition to the solar-cell-related activities covered in the previous section, a large effort is being made to investigate the basic properties of hydrogenated amorphous silicon and amorphous silicon alloy materials, light-induced effects, high deposition rates, and alternative deposition options.

Glow discharge deposition of amorphous silicon using higher order silane gases is being carried out at Brookhaven National Laboratory and Vactronics Corporation. The program is investigating optical and electronic properties of amorphous silicon produced at a deposition rate of at least 20 Å/s in the long term. The intrinsic amorphous silicon material presently being produced by glow discharge using silane gas is deposited at a rate of 2-4 Å/s. A deposition rate of 4 Å/s requires 42 min to grow a 1-μm-thick film, whereas a deposition rate of 20 Å/s would require only 8 min to grow the same film. Experimental data have already shown that glow discharge deposition using higher order silane gases can produce high-quality material at high deposition rates, greatly exceeding those obtained by the use of silane gas.

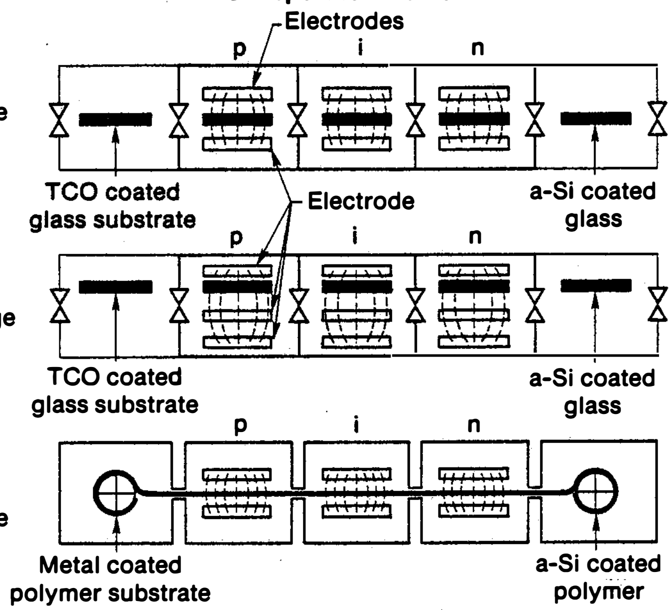
Light-induced effects are being studied at Oregon University, Massachusetts Institute of Technology, and Xerox Corporation. The effect of light soaking in a-Si:H samples deposited either in an ultra-high-vacuum (UHV) system or in a conventional deposition system has been studied by measuring the change in dangling bond density using electron spin resonance (ESR). Although the UHV-deposited samples have lower impurity levels (one to two orders of magnitude) than the impurity concentrations in conventionally deposited samples, the light-soaking effect was found to be nearly identical. This indicates that impurities play a minimal role in generating the light-induced effects in a-Si:H samples with normal impurity levels. The contribution of impurities to the density of light-induced defects is significant only when the impurity level in a-Si:H is higher than about 1%.

The potential of chemical vapor deposition (CVD) is also being evaluated. Both low-pressure (LPCVD) and atmospheric-pressure (APCVD) deposition methods are being investigated at Chronar Corp., at the Institute of

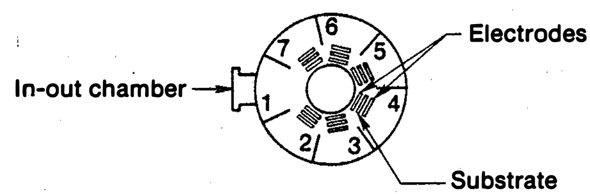
Three-year program goals are to demonstrate stable p-i-n solar cells of at least 12% efficiency, area of 1 cm²; demonstrate stable submodule of at least 8% efficiency, area of 1000 cm²; and establish technology base in amorphous silicon alloys leading to 18% efficiency in 1988.

Company	Approach
Chronar	• Single-junction p-i-n cells • RF glow discharge 2-electrode • 3 chambers • Glass substrate
Solarex	• Single-junction p-i-n cells • DC glow discharge 3-electrode • 3 chambers • Glass substrate
3-M	• Single-junction p-i-n cells • RF glow discharge 2-electrode • 3 chambers • Flexible polymer substrate
SPIRE	• Multi-junction a-Si alloy cells • RF glow discharge • 6 chamber • Glass substrate

a-Si Deposition Method



Three-Chamber Reactors for Depositing p-i-n Material



Six-Chamber Reactor for Depositing Material for Multi-Junction Cells

Figure 4. Technical Approaches of New Multi-Year Initiatives in Amorphous Silicon

Energy Conversion, and at Harvard University. Current studies are restricted to CVD using higher order silane gases. The higher order silane gases decompose at relatively low temperatures (less than 500°C), and, as a result, the films contain large amounts of hydrogen and can also be deposited at very high deposition rates. APCVD-prepared films have been grown at deposition rates above 50 Å/s, while LPCVD-prepared films were grown at rates up to 15 Å/s. Diagnostic Schottky barrier cells and p-i-n type cells were fabricated using material grown by both LPCVD and APCVD. Short-circuit current densities of 10 mA/cm^2 have been achieved, demonstrating good quality material. In addition, the optical bandgap of presently prepared material is reported to be 0.1-0.2 eV below that of glow-discharge-prepared material. The lower bandgap is more ideally suited for higher efficiencies than the glow discharge material. Light-induced effects in CVD-prepared films appear to be less than for glow-discharge-prepared films, although the films' quality has not yet reached that of glow-discharge-deposited films. CVD is widely used in the semiconductor industry, is readily scalable, is a simpler process than the glow discharge process, and could substantially reduce costs.

Stacking solar cells with different bandgaps in series optically and electrically captures more of the solar radiation. The individual cells in the stack can be made of various amorphous silicon alloy materials with passivators such as hydrogen or fluorine to achieve different optical bandgaps. Hydrogenated amorphous silicon has been studied extensively and is the basis around which the standard amorphous silicon stacked cell is designed. Materials being considered include a-SiGe:H and a-SiSn:H (both for the low-bandgap cell) and a-SiN:H (for the high-bandgap cell). The best results reported to date are for a two-layer a-Si:H material with two different thickness layers in series, and with a a-SiGe:H low-bandgap cell. The results reported (11) are 8.6% efficiency for an area of 100 cm^2 (V_{oc} = 2.22 V, J_{sc} = 6.41 mA/cm^2, FF = 0.604). Theoretical conversion efficiencies for the multibandgap cell are above 20%.

A newer type of solar device that is an outgrowth of the thin-film nature of these materials has recently been proposed. This new structure comprises amorphous materials (12) consisting of a superlattice of alternating layers 8-1200 Å thick of hydrogenated amorphous silicon alloys. The amorphous and thin-film nature of these materials opens research to a whole new class of compound materials not readily available in the past. This new technology has great potential in many areas, including highly efficient PV devices. Research in amorphous silicon alloy materials is being conducted at Harvard University, Xerox Corporation, North Carolina State University, and the Solar Energy Research Institute.

Among these research activities being conducted at universities and research laboratories, Harvard is developing materials that can reduce the electrical contact resistance between the transparent conducting oxide and the amorphous layers. Diffusion barriers are also being developed to prevent contaminants in glass substrates from affecting the performance of the transparent conducting layer. The Naval Research Laboratory is conducting Nuclear Magnetic Resonance (NMR) and Electron Spin Resonance (ESR) experiments on amorphous materials to determine the bonding configurations of boron and phosphorus in the doped amorphous materials. The University of Colorado is characterizing the plasma in glow discharge reactors to correlate various neutral radical species with film properties.

CONCLUSIONS

The DOE/SERI amorphous silicon program is now in its fifth year, and technological progress is continually increasing. As a consequence, the number of institutions and researchers involved and the number of scientific papers being published is expanding. Without question, advances have been primarily achieved by the efforts of dedicated experimenters. The mass production of amorphous-silicon-powered solar batteries at a current annual rate of about 80 million units has been one of the major events in the history of photovoltaics, and is a result of imparting the basic simplicity of photovoltaic technology to large groups of people with diverse interests and knowledge. It is clear that single-junction amorphous silicon solar cells will reach 12% efficiency in the next few years and then increase in efficiency at a slower rate. U.S. industry is now producing submodules near 5% efficiency (1000 cm^2 in area) on a laboratory scale. Modules consisting of one or more submodules are also being fabricated. A market for 3 MW_p of solar cells using amorphous silicon was reached in 1983, which is 15% of the total photovoltaic market. Amorphous silicon solar devices will continue to capture a larger share of the market in the future. The cost goal of \$1/W_p will be reached when the production volume reaches 50-100 MW_p per year. To reach this goal in 1988, however, a company producing 3 MW_p in 1984 would have to double its capacity each year for the next five years. The biggest obstacle to reaching this goal will be the availability of sufficient resources, particularly in a few more years. The challenge to the scientific community is to maintain a high quality of research in improving the characteristics of currently used materials, such as resolving the stability issue (the so-called Staebler-Wronski effect), solving problems associated with larger sizes, and substantially increasing the material deposition rate while maintaining good optoelectrical properties.

The second step in the long-term amorphous silicon research plan is to develop multijunction solar cells that achieve conversion efficiencies of more than 20%. This demands in-depth knowledge of amorphous silicon alloys to achieve the different optical bandgaps required for stacked solar cells. Research in amorphous silicon alloys is in its infancy. The opportunities are great and require the attention of the world's best scientists.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-83CH10093.

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