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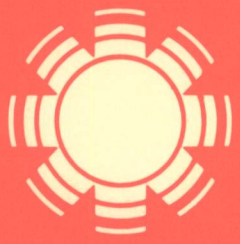
SERI Photovoltaics Advanced Research and Development: FY 1983 Accomplishments

Program Office,
Solar Electric Conversion
Research Division



SERI

Solar Energy Research Institute
A Division of Midwest Research Institute

1617 Cole Boulevard
Golden, Colorado 80401

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PREFACE

This document presents the accomplishments of SERI's research and development efforts in photovoltaics for the federal fiscal year 1983 (October 1, 1982, through September 30, 1983). In the same vein, the document contains a bibliography listing SERI-supported technical publications in photovoltaics that appeared in the same time period.

Researchers in SERI's Solar Electric Conversion Research Division are sincerely acknowledged for the managerial and technical efforts that have led to this listing of impressive accomplishments and publications. Finally, SERI's Technical Information Branch is gratefully acknowledged for compiling the bibliography.

Approved for

SOLAR ENERGY RESEARCH INSTITUTE

Donald Ritchie, Manager
Solar Electric Conversion Research
Division

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SECTION 1.0

INTRODUCTION

This summary of FY 1983 accomplishments contains the technical highlights of SERI's program in photovoltaics (PV) research and development and a bibliography of the resulting publications. Also included are several management highlights that arose from SERI's assessments of progress in these areas and tasks. SERI's participation in and chairmanship of a Thin Film Research Task Force appointed by the U.S. Department of Energy led to a strong recommendation for a new management structure consisting of technology offices possessing broad program and implementation responsibilities. Such an office was initiated at SERI for the amorphous silicon area and its implementation will be completed in early FY 1984. As a result of these activities, plus SERI's ongoing internal assessment, a multiyear cost sharing (federal-industry) initiative was begun in FY 1983 to spur industrial R&D in high-efficiency single-junction and multijunction amorphous silicon thin film solar cells. Phasing down of photoelectrochemical cell R&D was also begun in FY 1983. Finally, steps were taken to further develop internal capabilities for measurement and device analysis of solar cells and for the fabrication and modeling of devices.

The accomplishments are categorized according to SERI's subcontract R&D program areas (Amorphous Thin Films, Advanced High-Efficiency Concepts, Polycrystalline Thin Films, Polycrystalline Silicon, and Photoelectrochemical Cells) as well as to SERI's internal PV tasks (PV Devices and Measurements, Solid State Research, Insolation Resource Assessment, Advanced PV Systems Research, Performance Criteria/Test Methods Development, and the Lead Center).

SECTION 2.0

AMORPHOUS THIN FILMS

- *E. Sabisky, T. Surek, and J. Stone gave a presentation on amorphous silicon solar cells to Joseph J. Tribble, Assistant Secretary for Conservation and Renewable Energy, in Washington, D.C. on December 7, 1982. Two amorphous silicon RFPs were issued from SERI as a result of this presentation. The status of these two RFPs is given in the next two statements.

- *The amorphous silicon program's multiyear, cost-sharing initiative "Research on High-Efficiency Single Junction Monolithic Thin Film Amorphous Silicon Solar Cells" was decided. One subcontract was awarded and two other awards are in the final phase of negotiation. The subcontract to Chronar was awarded in September 1983.

- *The amorphous silicon program's multiyear, cost-sharing initiative "Research on High-Efficiency Stacked Multi-Junction Amorphous Silicon Alloy Thin Film Solar Cells" was completed. A subcontract to Spire Corporation was awarded in October 1983.

- *RCA Laboratories' large area amorphous silicon submodule performance surpassed the planned goals. This was the first submodule received from a subcontractor and tested at SERI. The outdoor test site measurement of 4.4% efficiency for the 350 cm^2 submodule was made by the Advanced Systems Research personnel. The subcontract goals called for an efficiency of 3% for a submodule of about 400 cm^2 in area.

- *Chronar Corporation's large area amorphous silicon submodule performance also was impressive. The SERI outdoor test site measurement was 4.6% efficiency for the 127 cm^2 submodule.

- *Researchers at Xerox Corporation made measurements on amorphous silicon materials which indicate higher short-circuit currents are possible. Electron drift mobility of 2.5 $cm^2/V\text{-}s$ on a thick sample (~5 μm) of undoped amorphous silicon was reported. Previously, the highest value was 1 $cm^2/V\text{-}s$.

- *Dr. R. Gordon of Harvard University measured the highest value yet for external short-circuit current density for chemical-vapor deposited (CVD) films deposited at high growth rates (~50 Å/s). The value of 10 mA/cm^2 on a platinum Schottky barrier solar cell was achieved by compensating for the optical losses in the platinum. The intrinsic amorphous silicon material was deposited by atmospheric pressure CVD.

- *HT Products, Inc., reported the greatest performance to date for a solar cell deposited on stainless steel (SS). The n(microcrystalline Si)-i-p/SS sample cell parameters reported were as follows: efficiency = 7.4%; V_{oc} = 877 mV; J_{sc} = 12.9 mA/cm^2; and FF = 0.65. With the inclusion of a textured back surface, efficiencies greater than 8% should be achieved.

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*Major accomplishments are denoted throughout this report by an asterisk.

- H. Wiesmann of HT Products, Inc., reported the highest open-circuit voltage to date for a PIN cell structure. This was 990 mV and is close to the maximum theoretical value calculated by T. Tiedje of Exxon. The previous high value of 969 mV was measured at SERI on one of Wiesmann's cells.
- RCA Laboratories reported conversion efficiencies as high as 8.5% for PIN cells fabricated in glow-discharge deposition systems used in the SERI subcontract at RCA. Efficiencies as high as 10.1% were reported for cells fabricated from other deposition systems at RCA Laboratories.
- Single-junction amorphous silicon solar cells were fabricated at Exxon Research and Engineering Co. using reactive sputtering deposition to grow the film. The cell efficiencies are 5.5% and 4.3% for areas of 2 mm^2 and 1 cm^2, respectively. The 5.5% efficient solar cell is the highest value reported for reactive sputtered films.
- The Amorphous Materials Subcontractors' Review Meeting was held in Washington, D.C., November 22-24, 1982. Seventy-five persons attended. In addition to presentations given by the SERI-funded subcontractors, there were three invited talks (two from Japan) and seven guest speakers from companies pursuing amorphous silicon research. There were also participants from the Basic Energy Sciences (BES) funded program.
- Xerox Corporation's studies on amorphous silicon alloy materials suggest the primary effect of light soaking is to introduce dangling bonds. Also, the $\mu\tau$ product for both electrons and holes is reduced by about an order of magnitude, showing that bulk deep traps are introduced due to light soaking.
- Researchers at the University of Colorado developed improved measurement apparatus and techniques. Results suggest that the SiH_3 radical may be the predominant radical precursor of glow discharge amorphous silicon film growth. Also, they have detected for the first time the presence of Si, SiH, SiH_2, and SiH_3 radical species in a dc proximity silane discharge.
- RCA Laboratories' research on a-Si rf (capacitive) glow discharge films suggests the addition of boron compensates for n-type impurities such as phosphorus. Before the addition of boron, depletion widths were about 0.1 μm. After boron doping, the sample became fully depleted; the space charge extending over the entire sample thickness (2.4 μm).
- RCA Laboratories also reported that their findings suggest that structural defects may be playing a dominant role in affecting diffusion lengths (L) rather than impurities such as O, N, and C. The structural defects may be related to the growth process or indirectly to impurities.
- Basic studies contracts to MIT and the University of Oregon on the origin of the Staebler-Wronski effect were initiated. The studies include theoretical modelling of light-induced effects and measurement techniques using Deep Level Transient Spectroscopy and Depletion Width Modulated ESR Spectroscopy.

- Dr. R.G. Gordon at Harvard University successfully developed atmospheric chemical vapor deposition of fluorine-doped tin oxide on glass substrates. This transparent conductive thin film technology was transferred to industry and is now commercially produced. The thin film is more stable and less expensive to deposit than indium-tin oxide.
- A comprehensive report by James Lorenz, SERI consultant, was published, entitled "A Survey of the Preparation, Purity, and Availability of Silanes." It presents data on current market size, cost, preparation, and purification methods of silanes. The report also discusses the effect of impurities on solar cell performance and presents information on current U.S. and Japanese commercial suppliers of silane and disilane. A separate section is devoted to the high-purity ultra-pure silane produced by Union Carbide's new pilot plant in Washougal, Washington.

SECTION 3.0

ADVANCED HIGH-EFFICIENCY CONCEPTS

- *Dr. J. Fan of MIT-Lincoln Laboratory reported that his group achieved 13% efficiency for GaAlAs solar cells grown on GaAs by MOCVD. This achievement surpasses the FY83 goal for 12% efficient cells.
- *The GaAsP materials system shows considerable promise for use in the top cell of a multijunction structure. In less than one year, MIT-Lincoln Laboratory initiated the study of GaAsP cells and achieved more than 11% efficiency.
- *Dr. J. Fan's group at MIT Lincoln Laboratory also demonstrated lateral overgrowth of GaAlAs for cleft-type processing.
- *Varian Associates fabricated high-efficiency GaInAs solar cells having a band gap of 1.15 eV. These cells would be appropriate for the bottom cell of a cascade structure or, since the efficiency drops slowly at high concentration, they may eventually serve to upgrade performance of conventional concentrator arrays. In outdoor testing, the cell achieved 21.5% efficiency at 172 suns and 21.4% efficiency at 380 suns.
- *S. Vernon of Spire Corporation reported the successful MOCVD growth of GaAs and AlGaAs (10% Al) directly on Si. This was the first such demonstration and it represents a major step in both thin film III-V cell development and in the development of multijunction flat plate cells (III-V's on Si). The initial runs showed good adhesion and no visible microcracking.
- *Another accomplishment by Dr. J. Fan's group was thin film GaAs on silicon substrate solar cells having 14.5% efficiency. This research effort was redirected to increase the emphasis on GaAlAs and GaAsP for use in a multiband-gap structure.
- Spire Corporation reported achieving 20.3% efficiency for AlGaAs/GaAs heteroface cells with AR coating. Cell parameter measurements were V_{oc} = 1.01 V, J_{sc} = 23.6 mA/cm^2, and FF = 0.85, at 1 sun illumination, AM1 spectra.
- Varian Associates' efforts towards development of a 30% multijunction solar cell progressed greatly. The use of bis-dicylopentadienyl-Mg instead of the traditional dopant Zn is the improvement for doping MOCVD grown material. When an AlGaAs grading layer and top cell structure are grown on a high-efficiency GaInAs cell, Zn rapidly diffuses and degrades the spectral response of the GaInAs cell. The use of magnesium avoids this problem. Test structures of Mg-doped AlGaAs on GaInAs indicate that the spectral response of the cell does not degrade.
- The design and construction of a plasma-enhanced MOCVD growth chamber were completed by United Technology, Inc. This reactor is expected to be able to grow GaAs at low temperatures (approximately 450°C) and test the concept of GaAs grown directly on NaCl.

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*Major accomplishments.

- Dr. J. Fan and C. Bozler of MIT Lincoln Laboratory were awarded a patent for "Solar Cells Having Ultrathin Active Layers" on March 8, 1983. The patent covers use of back-surface optical reflectors on thin solar cells of amorphous silicon and other materials.
- Laboratory facilities for research at Southern Methodist University were relocated to provide a safer, more efficient environment. The first efforts in the new facility evaluated the large grain polycrystalline films developed prior to the relocation. The new material increased the efficiency of polycrystalline GaAs homojunction solar cells to more than 9%, a significant improvement relative to the 8.1% achieved in FY 1982.
- A new program for modeling of III-V solar cells was initiated with Purdue University. Purdue will extend the capabilities of their existing computer codes to provide a tool for evaluation of novel, high-efficiency solar cell designs.
- Researchers at United Technologies significantly improved the quality of thin film germanium layers used for preparation of GaAs solar cells. To reduce the defect density in the germanium they perfected a polishing process for the NaCl substrates. An improved mechanical polish followed by a vapor etch eliminates all surface defects. After the germanium is separated from the NaCl, the layers are thermally annealed, which improves both the flatness as well as the strength of the thin film germanium.

SECTION 4.0

POLYCRYSTALLINE THIN FILMS

- *The formation of a joint venture company to develop thin film $CuInSe_2$ solar cells for commercial markets was a direct outgrowth of SERI-supported work and represents an important example of technology transfer. The new Seattle-based company, SOVOLCO, will be operated by the Boeing Engineering and Construction Company, which is in partnership with Reading and Bates Development Company of Tulsa, Oklahoma, a wholly owned subsidiary of Reading and Bates Corporation. Following the achievement of the successful deposition of high efficiency cells deposited on glass, a low-cost substrate, the Boeing/Reading and Bates Joint Management Committee approved the expenditure of funds for the second phase of the SOVOLCO venture. A pilot plant is expected to be operational in 1985.

- *Boeing Aerospace Company produced the highest efficiency non-single-crystal thin-film solar cell to date. Their 1-cm^2 CdZnS/$CuInSe_2$ cell was reported at 11% efficiency under ELH solar simulation (100 mW/cm^2), having cell parameters of V_{oc} = 0.437V, J_{sc} = 38.5 mA/cm^2, and FF = 0.653. The efficiency of a similar Boeing cell was verified at SERI at 10.5% at 25°C under 100 mW/cm^2 xenon solar simulation.

- *Southern Methodist University is investigating the deposition of p-type cadmium telluride films on W/graphite substrates using the direct combination of cadmium and tellurium in a hydrogen atmosphere containing a low concentration of oxygen. ITO/CdTe heterojunction devices were deposited with efficiencies up to 7.8%. The chemical vapor deposition research at SMU was moved to new off-campus facilities leased by the university.

- *K. Bachmann of North Carolina State University (NCSU) announced that Hall effect measurements on NCSU-grown n- and p-type $CuInSe_2$ single crystals showed room temperature mobilities of 920 cm^2/V-sec and 18.8 cm^2/V sec for electrons and holes, respectively--higher than any other mobilities reported for $CuInSe_2$.

- *Battelle Columbus Laboratories reported no intrinsic degradation for 12 $CuInSe_2$ cells fabricated by the Boeing Aerospace Company. This result confirms the preliminary studies performed at Boeing.

- *The University of Delaware, Institute of Energy Conversion (IEC), confirmed that effusion cell deposition CdS/$CuInSe_2$ cells have improved open-circuit voltages when the initial substrate temperature for $CuInSe_2$ deposition is 275°C. V_{oc} improvements of up to 20 mV were observed along with smoother surfaces for the two-layer composite films. IEC deposited CdS/$CuInSe_2$ cells of efficiencies up to 7.8%, using Knudsen cells for $CuInSe_2$ deposition.

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*Major accomplishments.

- *Stanford succeeded in depositing p-type CdTe by hot wall vacuum evaporation. The antimony-doped films are 2-3 microns thick, with 5×10^{15} carriers/cm^3, and a resistivity of about 100 ohm-cm. The deposition of p-type films allows fabrication of heterojunction devices with n-CdS whose AM1 device efficiencies have now reached 4.2%.

- S. Wagner of Princeton University reported two important observations in a study of ^{63}Cu NMR signals in $CuInSe_2$:

  -- Copper diffuses more slowly in $CuInSe_2$ than in other copper compounds such as Cu_2S. Preliminary estimates using NMR-derived Cu^+ diffusivities in $CuInSe_2$ suggest that neither copper nodule formation nor formation of traps in the CdS due to Cu^+ migration should be a problem in near-stoichiometric $CuInSe_2$ at normal operating temperatures. These findings increase our understanding of the stability of $CdS/CuInSe_2$ cells.

  -- A previously unreported phase-transition takes place in $CuInSe_2$ at 665°C.

- Westinghouse reported a surface treatment for CdS/Cu_2S solar cells that increases stability significantly. Untreated cells in the 5% to 6% efficiency range decayed exponentially with a time constant of 35 hours. A treated (unencapsulated) cell remained stable for 120 hours of illumination in flowing O_2/water vapor at room temperature. A patent disclosure is being filed with the DOE office in Chicago.

- K. Bachmann of North Carolina State University grew his first crack- and void-free $CuInSe_2$ single crystals (approximately 5 mm x 6 mm x 3 mm). Previous problems of the ingot sticking to its container were eliminated by using pyrolytic boron nitride (BN) boats, allowing single crystals to be grown by gradient freezing. Other growth methods (e.g., Bridgman) are being tried with the new boats, and vitreous carbon is being investigated as a less-expensive substitute for BN. High-quality crystals are being grown and distributed, including samples to SERI for surface analysis and to Boeing Aerospace for photoluminescence studies.

- PolySolar, Inc., reported the deposition of the first single-phase $CuInSe_2$ films by chemical vapor transport. 10-100 ohm-cm films were deposited onto both alumina and graphite substrates. $ZnO/CuInSe_2$ devices were fabricated with up to 400 mV open-circuit voltages, but currents are as yet low due to the high sheet resistance of the ZnO.

- Colorado State University reported measurements of light-induced changes in the $CdS/CuInSe_2$ barrier. This barrier shift reduces device open-circuit voltage by more than 100 mV.

- Telic Corporation reported the achievement of a 4% efficient reactively-sputtered $CuInSe_2$ cell.

- An assessment of hot wall vacuum evaporation (HWVE) was written. The study recommends redirection of in-house HWVE with emphasis on doping, contacting, and device studies.

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*Major accomplishments.

- An assessment of $Cu_{2-x}Se$ PV research was written. The study recommends that, lacking a breakthrough in the current subcontract with Boeing Aerospace Company, research should be terminated in $Cu_{2-x}Se$ because of low cell efficiency and poor stability. Boeing developed an initial $Cu_{2-x}Se/ZnSe/CdS$ device using 0.5 micron of ZnSe with initial photoactive response about 4% efficiency and no Cu nodule growth.
- Colorado State University reports the deposition of thin-films of p-CdTe using both a conventional three-electrode potentiostatic technique and an electrodeless approach. The research was transferred to the University of Texas at Arlington following the principal investigator's acceptance of a faculty position there.
- Analysis of I-V data taken at the Joint Center for Graduate Studies, University of Washington, on Boeing $CuInSe_2$ cells shows that the diode quality factor varies inversely with temperature, yielding a dark diode current that depends exponentially on voltage and has only a weak temperature dependence. These data are consistent with multi-step tunneling recombination at the heteroface. Suggestions for avoiding this efficiency limitation experimentally are under consideration.

SECTION 5.0

POLYCRYSTALLINE SILICON

- *Spire Corporation fabricated high-efficiency silicon solar cells achieving the planned FY 1983 goal of exceeding 17% efficiency. SERI verified the cell measurements with the two highest efficient cells exhibiting 18% efficiency on 4 cm^2 area, with parameters of V_{oc} = 622 mV, J_{sc} = 36.1 mA/cm^2, and FF = 0.80.
- *Westinghouse Electric Corporation R&D Center similarly achieved the goal of exceeding 17% efficient silicon solar cells. Cell parameter measurements were verified at SERI.
- *Energy Materials Corporation achieved the demonstration of growing silicon solar cell material at high throughput and high cell efficiency capability. Low angle silicon sheet (LASS) ribbon blanks grown in excess of 200 cm^2/min (37 cm/min) were processed using SERI baseline cell fabrication techniques. Results included a 12.7% efficient cell (14.4% efficient control Cz cell). Electron channeling analysis showed that the planar material is single crystalline and the dendritic material is polycrystalline.
- *The University of Washington Joint Center for Graduate Studies fabricated a single-crystal metal-insulator-n-p (MINP) solar cell exhibiting 15.4% efficiency. This is a significant improvement over the 11.7% efficiency they achieved last year. The SERI measurements for the 15.4% efficient cell are 3.97 cm^2 area, V_{oc} = 626 mV, J_{sc} = 31.5 mA/cm^2, and FF = 0.78.
- Westinghouse Electric Corporation R&D Center and SERI collaborated to examine hydrogen passivation technology, which showed up to a 29% relative improvement in cell efficiencies (7.56% to 9.09%) for non-AR coated cells. This research examines cells having only bulk and point defects and no grain boundaries. This work is continuing.
- A. D. Little developed a method for improving the uniform thickness and reducing the stress along the width and length of silicon ribbon grown by the edge-supported pulling (ESP) method. The use of melt circulation and movable radiation shields was instrumental in accomplishing these results.
- SERI, in collaboration with JPL, conducted a silicon ribbon growth assessment. The results were communicated to DOE, and SERI's ribbon growth efforts are being transferred to JPL.
- SERI, in collaboration with A. D. Little, confirmed that during hydrogen passivation of ESP cells the silver front contact removal is the cause of a reduction of the fill factor. After A. D. Little had again silver-plated the hydrogen passivated cell, the fill factor recovered to its prehydrogenation level of 0.76 while the current and voltage improvements due to the passivation were maintained.

*Major accomplishments.

- Five excimer laser-processed single-crystal silicon solar cells fabricated by Rosa Young at ORNL and Helionetics were measured at SERI. The best cell was 16.4% efficient under AM1 illumination. SIMS measurements of the dopant profiles of excimer laser-processed solar cells were also performed by the SERI Devices and Measurements Branch.

SECTION 6.0

PHOTOELECTROCHEMICAL CELLS

- *Long-term stability measurements were performed at Grumman Aerospace on thin-film CdSe/polysulfide photoelectrochemical cells. A 4.8% efficient cell was run continuously at maximum power for 26 weeks with less than a 1% decrease in power output. An addition of 0.05 M Se to the standard polysulfide electrolyte contributed to the excellent stability behavior observed.

- *Grumman improved the fill factor of n-CdSe films deposited on titanium substrates in electrochemical photovoltaic cells by using two sources containing cadmium selenide and selenium. A 7.08% efficiency was achieved with the following cell parameters: J_{sc} = 15 mA/cm^2; V_{oc} = 0.59 V; and FF = 0.60 (75-mW/cm^2 ELH lamp simulator). This result represents a nearly 10% improvement in the state-of-the-art efficiency for thin film, n-cadmium selenide, electrochemical photovoltaic cells incorporating a sulfide/polysulfide electrolyte.

- *The DOE-Texas Instruments Solar Energy Systems cooperative program was successful in establishing technical feasibility for the components of a hybrid photovoltaic/thermal system with electrochemical storage. Also, the program identified the risk factors involved with developing the technology to a commercial product.

- *SRI, Inc., developed photoelectrochemical cells having 9.9% efficiency. This was for II-VI polycrystalline thin film materials and was a CdSe/ferro/ferricyanide thin film materials system. The control cell of single-crystal materials was 12.4% efficient. The stability of the thin film cells was from a few hours to a few days.

- The Sixth Photoelectrochemical Cell Contractors' Review meeting was held in the Denver area on February 24-25, 1982. The meeting consisted of presentations by SERI in-house researchers, photoelectrochemical subcontractors, and an invited presentation by Texas Instruments.

- Weizmann Institute of Science reported a significant increase in the solar conversion system efficiency from 2.6% to 3% for a 10-mW, three-electrode, in situ storage cell. The system could become competitive with the Texas Instruments Solar Energy Photovoltaic/Storage System. Results indicate that significantly higher system efficiencies are achievable in principle as more efficient, higher voltage thin film electrodes become available. The photoelectrode currently is $CdSe_{1-x}Te$ at 3.3% coversion efficiency. The storage electrode is Sn/SnS. Voltage efficiency was 90% and the current efficiency was 100%. Output voltage was 0.4 V at a discharge current density of 1 mA/cm^2. The energy density was 9 W h/kg.

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*Major accomplishments.

SECTION 7.0

PV DEVICES AND MEASUREMENTS

- *The PV Devices and Measurements FY 1983 program included the evaluation of nearly 1000 materials and device samples. These included internal R&D and external DOE/SERI-sponsored research. Evaluations ranged from determination of composition to cell efficiency and spectral response determination. Verification of 18% efficiency for crystal silicon solar cells and measurements of composition and electrical properties of (CdZn)S/$CuInSe_2$ interfaces are examples of the evaluations made.
- *Researchers at SERI discovered, via EBIC studies on unbaked, oxygen heat-treated and vacuum heat-treated (CdZn)S/$CuInSe_2$ cells that demonstrated relationships exist between the annealing procedures and heterojunction activation. Significant increases in efficiency are directly related to the oxygen treatment, rather than to the junction activation process that occurs in any thermal processing.
- *Researchers at SERI correlated the chemical and electro-optical effects of grain boundaries in polycrystalline silicon cells. The relationship between oxygen segregation at heat treatment above 650°C and grain boundary electrical activation was reported. The penetration of hydrogen along grain boundaries as a result of passivation processing was measured for the first time.
- *Minority carrier lifetimes were measured directly for the first time ever in CdTe, CdSe, and InP using picosecond laser spectroscopy techniques developed in the PV Devices and Measurements Laboratories.
- *Fabrication and testing of the EBIC hot stage for the SEM (scanning electron microscope) was completed. This allows for monitoring the change in the electrical activity of a device during heat treatment. Initial applications were made to the in situ, real-time observation of the electrical response of the Mo/$CuInSe_2$ and CdS/$CuInSe_2$ junctions from room temperature to 250°C.
- L. L. Kazmerski participated in a cooperative research visit to Brazil, sponsored by the Brazilian Council (CNPq) and funded by the Organization of American States (July 8-August 6, 1983). Technical interactions were established with the Instituto Militar de Engenharia (IME) in Rio de Janeiro, with projects in cell measurements, CdS/$CuInSe_2$ cells, SnO_x:Sb/poly-Si devices, Cu_2S/CdS, and a-Si:H devices. The work involved the establishment of cell performance evaluation systems for IME, and the fabrication of material/devices for thin film technologies. IME will continue the cooperation by sending a scientist to SERI in Spring 1984 to support characterization research.

*Major accomplishments.

- The effects of heat treatment in oxygen, nitrogen, argon, and high vacuum on the optical properties of $CuInSe_2$ films were investigated. Annealing in oxygen or inert atmospheres improves the absorption characteristics. Heating (approximately 200°C) at 10^{-8} torr causes Se depletion from the film surface and severely degrades the absorptance.
- The SERI PV Devices and Measurements Laboratories booklet was published and distributed to members of the PV community. The booklet introduces the functions, capabilities, and interrelationships of the four laboratory research areas. These areas are cell performance, electro-optical characterization, materials characterization, and surface and analysis research. The booklet is available from SERI.
- Cooperative research efforts included more than 50 projects with DOE/SERI-sponsored subcontractors and internal SERI researchers. This resulted in joint publication of some 20 papers with cooperating groups.
- Internal research accomplishments included the development or improvement of various measurement systems or methods. These included the development of the Deep Level Transient Spectroscopy system, the photoluminescence (high resolution) facility, in situ temperature-dependent EBIC on SEM, a method for topographical corrections for AES and EBIC signals, and a method and hardware for isolating interfaces in PV devices using SIMS/ion etching.
- Program support accomplishments included the implementation of the outdoor cell measurement facility, extending the spectral response measurement capabilities to 1.5 μm, and developing a high-resolution, multiple-detection digital laser scanner for device investigations.
- X-ray photoelectron spectroscopy was utilized to evaluate the effects of various surface treatments on $CuInSe_2$. One experiment showed that Ar^+ ion bombardment induces preferential sputtering of copper from the $CuInSe_2$ system. Initial experiments with a BrMeOH etch on $CuInSe_2$ indicate that a depletion of the Cu also exists for this treatment.
- Preliminary investigation of the Cu variation in the two-layer $CuInSe_2$ of the $Cd(Zn)S/CuInSe_2$ heterojunction was done. Early Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) results reported no variation within the 0.1 atomic percent resolution of these techniques. Virgin and heat-treated cells are being compared using these techniques and secondary ion mass spectrometry (SIMS). Ball-cratered samples provided by Boeing show excessive damage due to this film depth exposure technique. AES line scans have shown no variation in the Cu within the $CuInSe_2$ layers.
- Transmission electron microscopy (TEM) was successfully used to measure dislocation densitites of Ge films grown on Si wafers at SMU. An improvement of three orders of magnitude was observed when using a graded layer of Ge.
- PV Devices and Measurements researchers are currently working with the Spire Corporation to develop a GaAs standard cell for use in verifying cell performance measurements.

- P. Sheldon and R. Ahrenkiel were given the SERI Outstanding Achievement Awards for their contributions to understanding mechanisms limiting heterojunction performance. They were also recognized by the American Vacuum Society (AVS) for an outstanding poster session at the 1982 AVS symposium. Also, P. J. Ireland received a SERI Outstanding Performance Award for his research contributions and dedication to the Institute.
- The researchers in the PV Devices and Measurements Branch published about 80 articles on their FY 1983 work.
- More than 110 individual technical visitors or groups toured the PV Devices and Measurements research facilities. This included scientists and managers of either U.S. or foreign governments, institutions, or companies.
- Four visiting professors conducted research at SERI in the PV Devices and Measurements Branch.

SECTION 8.0

SOLID STATE RESEARCH

- *The Solid State Theory group has (1) calculated the electronic structure of all substitutional and interstitial 3d transition metal impurities in silicon, explaining many of the relationships between material properties and electronic structure; (2) calculated the first self-consistent band structures of $CuAlS_2$, $CuGaS_2$, $CuInS_2$, $CuAlSe_2$, $CuGaSe_2$, and $CuInSe_2$, analyzing the band-gap anomalies; and (3) studied the properties of metal-semiconductor interfaces for III-V semiconductors, elucidating the mechanisms for Fermi energy pinning.

- *An efficient, low-cost chemical vapor transport (CVT) process for purifying metallurgical-grade silicon was invented at SERI. The process makes use of a modified Siemens-type reactor. The highest growth rate, 0.92 g/h, was obtained at the following conditions: alloy temperature = 700°C, total pressure = 650 torr, and Cl/H = 0.7. Impurity analysis by spark source mass spectrometry shows that the refined silicon contains undetectable amounts of boron and trace quantities (less than 1 ppm) of Al, P, Fe, and Cu. The material is n-type with a resistivity of 0.5 ohm-cm.

- *12.2% efficient solar cells were fabricated at SERI from recrystallized, electrorefined silicon. The recrystallized silicon was n-type with a resistivity of 0.1 ohm-cm. A control cell, consisting of a coprocessed n-type, 1.3 ohm-cm Czochralski wafer, had an efficiency of 11.9%, indicating that the electrorefined material is of relatively high quality.

- *The first superlattice structure with compositional matching adequate for a reduced dislocation density cascade cell was grown by MOCVD. The composition was determined by electron probe microanalysis. The structure consisted of a GaAs substrate; 10 microns on $GaAs_{1-x}P_x$ graded from x = 0 to x = 0.24; twenty (approximately 400-Å) periods of $GaAs_{1-x}P_x/GaAs$ superlattice with x_{avg} = 0.21; and a top layer of $GaAs_{.76}P_{.24}$. Planarity of the superlattice for x ≥ 0.2 remains a problem which appears to be unique to the MOCVD process and not inherent in the superlattice itself.

- *The complete new device process for fabricating shallow homojunction $n^+/i/p/p^+$ GaAs cells at SERI was worked out and nearly finalized. The two major steps developed were the electroplating of tin contacts and the successive anodization of the n^+ layers. Whereas SERI's best previous CVD cell was approximately 8% efficient, the first cell processed reached 13.6%. The maximum observed values of the cell parameters were V_{oc} = 0.954 V, J_{sc} = 19 mA/cm^2, and FF = 0.81.

- *Dislocation-free silicon crystals in both (100) and (111) orientations were grown from a cold crucible in an argon ambient with 470 kHz RF heating. This is the first time that dislocation-free growth was achieved with this method. The (100) crystal was doped with boron to 5×10^{16} atoms/cm^3 for solar cell evaluations. The undoped (111) crystal

*Major accomplishments.

had a residual 6 x 10^{13} atoms/cm^3 n-type background doping level, indicating very clean growth conditions. The crystals were approximately 12-15 mm in diameter.

- *Liquid encapsulated synthesis (LES) was applied, for the first time, to synthesis of $CuInSe_2$ from the elements. The compound was very close to ideal stoichiometry, as measured by Auger and electron-probe analysis. The ingot was 55mm in diameter and weighed 140 g. Single grains over 1 cm in size were present. However, the ingot was permeated with macro- and microcracks. Synthesis was carried out in a quartz crucible. An improved crucible design was made and crucibles of PBN were ordered to help alleviate the macrocracking problem. The ingot was n-type with resistivity in the 0.7-1.9 ohm-cm range. Qualitative SIMS analysis detected no major impurities.
- Preliminary results for liquid encapsulated Czochralski (LEC) growth of $CuInSe_2$ were also achieved and the technique appears to be viable.
- *A high-pressure crystal growth apparatus for the melt growth of compound semiconductors with volatile components (As, Se, P, etc.) was used for InP and $CuInSe_2$ growth.
- A new method for continuous casting of square cross-section silicon ingots was invented and reduced to practice. Very clean, large-grained ingots were obtained up to 25 mm x 25 mm x 170 mm in size. The system accepts a variety of feed stock geometries.
- A series of silicon sheet bicrystals were grown for electrical characterization of controlled grain boundaries via spreading resistance and mesa PV cell analysis.
- The growth rate and anisotropy of growth rate for silicon dendrites propagating on the free surface of a super-cooled melt were studied at SERI by enhanced-speed 16-mm movies. Growth rates on the order of 3 m/min and growth rate anisotropies on the order of 35 were recorded. The subsequently frozen melts were preserved for crystallographic analysis.
- Radial growth anisotropies and limiting growth forms of point-nucleated dislocation-free silicon sheets spreading horizontally on the free surface of a silicon melt have been measured for (100), (110), (111), and (112) sheet planes. Movie photography (16 mm) was used to record the growth process. Qualitative Wulff surface free energy polar plots were deduced from the growth shapes for each sheet plane. Analysis of the sheet edges has led to predicted geometries for the tip shape of unidirectional, dislocation-free, horizontally grown sheets growing in various directions within the above-mentioned planes.
- *The dark conductivity (σ_D) and photoresponse ($\mu\tau$ product) were evaluated for a series of a-SiSn:H alloy materials, which vary in band gap from 1.8 eV to 1.1 eV. The materials were fabricated in an RF glow discharge apparatus using mixtures of (a) SiH_4,H_2 and $SnCl_4$, and (b) SiH_4,H_2 and $Sn(CH_3)_4$ gases. The reduction in band gap is accompanied by a drastic decrease in the $\mu\tau$ product and an initial reduction in σ_D. These alloys

*Major accomplishments.

undergo an n-type to p-type conductivity transition with increasing Sn concentration. This was confirmed by thermopower measurements on samples of low band gap (high Sn concentration). This transition satisfactorily explains the σ_D and $\mu\tau$ data. The fact that almost identical results are obtained for the two sets of gases suggests that the presence of Sn, rather than Cl or C, in the films causes the transition.

- *Considerable progress was made in understanding the fabrication of p-i-n a-Si junctions. The junctions are fabricated for diagnostic purposes in the following configuration: stainless steel/p^+/i/n^+/Al, with the light entering through the n^+ region. While this is not an optimum configuration, it allows one to judge the quality of the junction. For instance, junctions with six orders of magnitude rectification at 0.8 V ($\sim V_{bc}$) are now fabricated. This is a direct measure of the p^+/i interface indicating a formation of an abrupt junction; i.e., there is very little contamination due to B in the active layer which creates an increase in the localized states leading to an excess current. This interpretation is borne out by SIMS results of the B profile. These types of diodes exhibit the following light characteristics: V_{oc} = 0.8-0.82 V, FF = 0.65-0.70, and J_{int} = 13-14 mA/cm^2, with internal efficiency approximately equal to 7.6%. An achievement of a FF of 0.7 is an indication that the device is fully depleted and is a direct consequence of a low density of states possessed by the material.

- *A p-type CdTe thin film was electrodeposited in situ on thin film CdS/ITO, forming a heterojunction. This is the first time CdTe thin film has been electrodeposited p-type. The measured parameters were: V_{oc} = 525 mV, I_{sc} = 21 mA/cm^2, and FF = 25%. The cell exhibited high series resistance.

- An n-CdTe/Au solar cell prepared by hot wall vacuum evaporation and 2.2% efficiency, with the following device parameters, was achieved: V_{oc} = 0.46 V, J_{sc} = 9.2 mA/cm^2, and FF = 52%.

- *CdS/$CuInSe_2$ thin film solar cell with an active area efficiency of 7.2% was achieved.

- *A correlation between stoichiometry and carrier concentration was established for $CuInSe_2$ thin films deposited by three-source evaporation.

- Device quality n- and p-type $CuInSe_2$ thin films with carrier concentrations ranging from 10^{13} - 10^{20} cm^{-3} were prepared and Hall mobilities greater than 100 cm^2/V-sec were achieved.

- The in-house research program coordinated by D. Cahen (visiting scientist from the Weizmann Institute) recently demonstrated that n-$CuInSe_2$ single crystals in aqueous iodine/iodide electrolytes can achieve efficiencies up to 11.7% for electrochemical photovoltaic cells. The results also have implications for establishing the potential for high efficiencies in solid state cells for this material.

- The electrochemical decomposition mechanism(s) of n- and p-$CuInSe_2$ photoelectrodes were determined under dark and light conditions in aqueous and nonaqueous electrolytes. These results have implications for solid state

*Major accomplishments.

devices. An electrolyte composition was developed for diagnostic photoelectrochemical devices for the investigation of the photoactivity of $CuInSe_2$ materials. For a family of compounds chemically related to $CuInSe_2$, the solid state and structural chemistry program on $(Cu_2Se)_x(In_2Se_3)_{1-x}$ phases was completed with the identification of several new modes of Se-stacking.

- *Device processing capabilities improved dramatically over the last year. Assistance was provided to the Si purification group where a baseline p/i process above 12% was achieved. The n/p process was improved to above 14% and was used extensively on processing of the crystals produced by the Crystal Growth Group. By incorporating surface passivation in the process, cell efficiency improved to 15.5%. GaAs processing support to the materials efforts of the High Efficiency Materials Group included utilizing lithography and other advanced techniques. Basic research into a silver contact system for GaAs was also conducted, resulting in a patent application being filed. Routine service to the other groups in the forms of metallization and photolithography of samples also was performed.
- The researchers in the Solid State Branch published about 50 articles on their FY 1983 work.
- More than 50 individual technical visitors or groups toured the Solid State research facilities. These included scientists and managers from U.S. and foreign governments, institutions, and companies.
- Six visiting professors, two post-docs, and two other scientists conducted research at SERI in the Solid State Research Branch.

*Major accomplishments.

SECTION 9.0

INSOLATION RESOURCE ASSESSMENT

- *A new insolation prediction model for cloudy sky conditions has been developed as a result of comparing four existing models (ERSATZ, MAC, CEM, and ASHRAE) with insolation data from the new National Weather Service solar radiation monitoring network (35 stations).
- *The computer analyses of errors associated with the SOLMET/ERSATZ historical data base (insolation estimating algorithms), utilizing four years of new insolation data, have been completed for 19 SOLMET and 14 ERSATZ sites. These results show that the existing U.S. historical data base has systematic errors ranging from 10% to 30%, depending on location and cloud conditions.
- All buildings for the new SERI Insolation Research Assessment Laboratory have been relocated and installed at the permanent test site on top of South Table Mountain.
- SERI-developed sun photometers (hardware and software) were prepared for extensive intercomparison during October 1983 with sun photometers from all over the world at the National Oceanic and Atmospheric Administration (NOAA) in Boulder, Colorado.

*Major accomplishments.

SECTION 10.0

ADVANCED PV SYSTEMS RESEARCH

- *The outdoor SERI PV test facility was relocated from the interim to the permanent SERI field test site and testing operations resumed. The facility testing capabilities were expanded to include long-term outdoor PV cell/module stability testing and performance testing (I-V measurements, efficiency, etc.). PV systems outdoor simulation testing was performed on advanced PV cells and modules at power levels up to 10 kW.

- *Research support to the amorphous silicon task in the form of outdoor testing of amorphous silicon submodules provided the test data used in verifying a major milestone in the PV program (see large area cell efficiency milestone achievement in the amorphous silicon section). In addition, projects in amorphous silicon conceptual module design, laser scribing, and manufacturing cost analysis were completed.

- *Outdoor long-term stability testing at SERI of CdS/$CuInSe_2$ solar cells was initiated in support of the Polycrystalline Thin Film program area. Earlier work performed by Battelle Columbus Laboratories under subcontract to SERI for indoor controlled stability tests provided important results (see polycrystalline thin film section on CdS/$CuInSe_2$ stability milestone) and testing techniques and allowed a smooth transition of test operations to SERI.

- Technical support in the form of testing, analysis, and evaluation of the TISES "D" Texas Instruments Solar Energy system project was provided at SERI, at Texas Instruments (Dallas, Texas), and at DOE headquarters.

- Projects on the design analysis of advanced PV technologies, an advanced PV module costing manual, and R&D decision methods were completed and reports published.

*Major accomplishments.

SECTION 11.0

PERFORMANCE CRITERIA/TEST METHODS DEVELOPMENT

- *Standards development work in ASTM's E-44.09 subcommittee is based on PV Program technical results that have been transferred through the SERI Performance Criteria/Test Method (PC/TM) task. S. Hogan is Acting Chairman of this subcommittee and G. Nuss is Vice-chairman, Energy Technologies, for the full committee, E-44. Two standards have passed Society Ballot, two passed Committee Ballot and will go to Society Ballot, and three are prepared for Committee Ballot.

- *IEEE PV standards activity was initiated through a SERI PC/TM subcontract. Subsequent technology transfer and participation in various consensus standards writing work resulted in the start of four IEEE PV systems standards and two of these will go to the IEEE Standards Board for approval as IEEE Standards.

- *Article 690 "Solar Photovoltaic Systems" was adopted for the 1984 National Electrical Code (NEC) by hand vote at the 87th Annual Meeting of the National Fire Protection Association (NFPA). Article 690 was developed under SERI contract by Underwriters Laboratories, Northbrook, Illinois, and is the first electrical PV code to be approved by a national code-setting body. The article includes a general section with definitions as well as technical sections covering circuit requirements, disconnection, wiring methods, grounding, marking, and connections to other electrical sources.

- The subcontractor report on "Safety Inspection Guidelines for Photovoltaic Residences" was completed early in FY 1983.

- International cooperation and exchange of information on PV issues, concepts, and technology was fostered by another subcontract to IEEE. Under this subcontract, IEEE manages and administers secretarial responsibilities for the International Electrotechnical Commission PV Technical Committee (IEC TC-82). IEEE also coordinates and supports U.S. technical participation in IEC TC-82. In FY 1983, the U.S. Technical Advisory Group met twice and U.S. delegates attended four working group meetings.

*Major accomplishments.

SECTION 12.0

LEAD CENTER ACTIVITIES

- *C. E. Witt, A. M. Hermann, and E. Sabisky participated in the Thin Film Research Task Force group, appointed by R. Annan to review DOE's role in the R&D of thin film PV technologies. C. E. Witt was the chairman. Other participants included Don Bickler and Bob Ferber from JPL and Eldon Boes from Sandia. The two major recommendations of this Task Force are (1) the primary emphasis of the amorphous silicon and polysilicon crystalline thin film research and development programs should be materials research, cell R&D, and submodule R&D through 1986; and (2) a new management structure should be established consisting of technology offices possessing broad program definition and implementation responsibilities for the primary collector technologies.
- *The FY 1984 Annual Operating Plan for SERI's AR&D project was developed, the review comments from DOE were incorporated, and the Plan sent to DOE on September 12, 1983. The AOP is responsive to the DOE National Photovoltaics Program: Five-Year Research Plan.
- The SERI PV Advisory Committee met August 2-3, 1982, to review SERI's internal research activities. Attending the review were J. Fan, C. Gay, R. Little, F. Russell, W. Spicer, R. Taylor, and J. Wise. Committee recommendations were considered for incorporation into SERI's research effort.
- J. Stone participated on the Electric Power Research Institute (EPRI) Advisory Committee at a Photovoltaic R&D Status and Outlook Workshop held in Palo Alto, California, December 14-15, 1982.
- The 5th Annual Review Meeting of the SERI PV AR&D Program was held in Denver, Colorado, May 19-21, 1982. Approximately 175 participants from government, national labs, industry, universities, utilities, and the public sector participated in the 2-1/2 day meeting, which consisted of research talks, invited panel discussions, and contributed poster papers from SERI subcontractors and in-house researchers.
- The solicitation for New Ideas for Photovoltaic Conversion resulted in 100 responses which were evaluated. Ten proposals in the competitive range were considered, and awards will be made early in FY 1984.

*Major accomplishments.

SECTION 13.0

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