

**SERI/TP-211-3595  
UC Category: 270  
DE89009506**

# **U.S. Polycrystalline Thin Film Solar Cells Program**

**H. S. Ullal  
K. Zweibel  
R. L. Mitchell**

**November 1989**

Prepared for the  
Materials Research Society  
1989 Fall Meeting  
Boston, Massachusetts  
27 November - 2 December 1989

**Prepared under Task No. PV940301**

**Solar Energy Research Institute**  
A Division of Midwest Research Institute

1617 Cole Boulevard  
Golden, Colorado 80401-3393

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

## NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

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

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issue of the following publications which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

## U. S. POLYCRYSTALLINE THIN FILM SOLAR CELLS PROGRAM

**HARIN S. ULLAL, KENNETH ZWEIBEL, AND RICHARD L. MITCHELL**  
Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401, U.S.A.

### ABSTRACT

The Polycrystalline Thin Film Solar Cells Program, part of the United States National Photovoltaic Program, performs R&D on copper indium diselenide and cadmium telluride thin films. The objective of the Program is to support research to develop cells and modules that meet the U.S. Department of Energy's long-term goals by achieving high efficiencies (15% - 20%), low-cost (\$50/m<sup>2</sup>), and long-time reliability (30 years). The importance of work in this area is due to the fact that the polycrystalline thin-film CuInSe<sub>2</sub> and CdTe solar cells and modules have made rapid advances. They have become the leading thin films for PV in terms of efficiency and stability. The U.S. Department of Energy has increased its funding through an initiative through the Solar Energy Research Institute in CuInSe<sub>2</sub> and CdTe with subcontracts to start in Spring 1990.

### INTRODUCTION

The Polycrystalline Thin Film Solar Cells Program is part of the United States National Photovoltaic Program. Other areas of research and development included in the national program are the fundamental and supporting research, flat plate thin-films, flat plate crystalline silicon, and concentrator cells [1].

**Table I: Polycrystalline Thin Films Program Participants**

Research Organization	Objective
ARCO Solar	High efficiency CuInSe <sub>2</sub> , 900 to 3900 cm <sup>2</sup> modules
Boeing Aerospace & Electronics	Evaporated CuGaInSe <sub>2</sub> cells, 100 cm <sup>2</sup> submodules
Institute of Energy Conversion	Evaporated and selenized CuInSe <sub>2</sub> ; CdTe cells; device modeling
International Solar Electric Technology	E-beam/sputtering Cu,In layers and selenization; 50 cm <sup>2</sup> submodules
University of Illinois	Sputtered/evaporated CuInSe <sub>2</sub> cells
University of Arkansas	Laser-processed Cu/In/Se films made by electroplating or sputtering
California Institute of Technology	Contact investigation of CuInSe <sub>2</sub> /Mo interface
Solar Energy Research Institute	Growth, characterization and device fabrication of CuInSe <sub>2</sub>
Colorado State University	Characterization and modeling of CdTe and CuInSe <sub>2</sub> cells
AMETEK	Electrodeposition of n-i-p CdS/CdTe/ZnTe cells and 100 cm <sup>2</sup> submodules
Photon Energy	Spraying of 900 to 3900 cm <sup>2</sup> CdTe modules
University of South Florida	Close space sublimation of CdTe cells; MOCVD of HgZnTe for top cells
Georgia Institute of Technology	MOCVD of CdTe and Cd <sub>1-x</sub> Zn <sub>x</sub> Te cells

The objective of the Polycrystalline Thin Film Solar Cells Program is to support research to develop cells and modules that meet the U.S. Department of Energy's long-term goals by achieving high efficiencies (15% - 20%), low-cost (\$50/m<sup>2</sup>), and long-time reliability (30 years). This paper covers the various research aspects of the subcontracts program in the polycrystalline thin film area. Table 1 summarizes the various research activities with the corresponding objectives of each of the subcontracts. The two main materials of interest are copper indium diselenide (CuInSe<sub>2</sub>, CIS) and cadmium telluride (CdTe). Specific research areas include fundamentals, modeling, characterization, measurements, device design, solar cell fabrication, module design and development, module processing, and stability of both CuInSe<sub>2</sub> and CdTe [2]. Figure 1 shows the progress of the polycrystalline thin film module technology in the past few years.

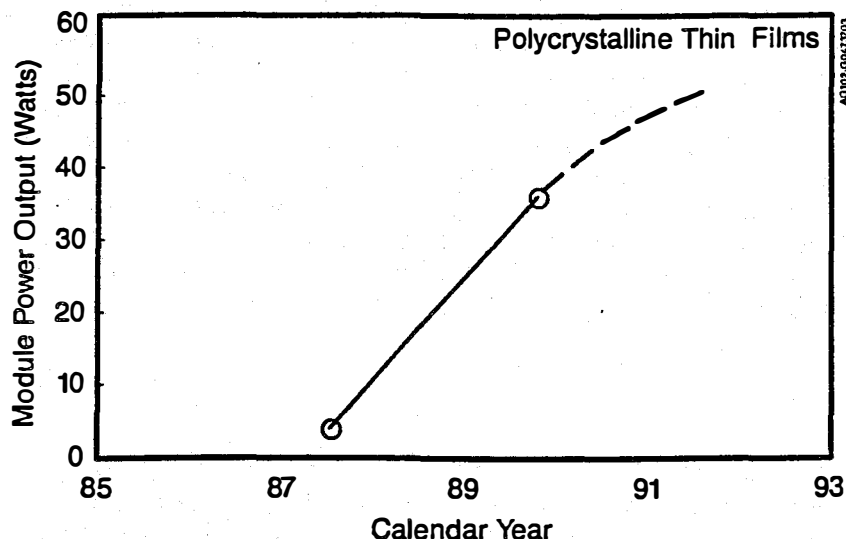


Figure 1 Progress of polycrystalline thin film module power output versus calendar year

## COPPER INDIUM DISELENIDE

During the past decade, CuInSe<sub>2</sub> has made significant technical progress and is now considered the leading candidate thin-film photovoltaic material in terms of efficiency and long-term reliability of these devices [3].

Wagner and co-workers at Bell Labs first fabricated 12% efficient CuInSe<sub>2</sub> single crystal cells in 1974 [4]. Single crystals are expensive for practical applications. Nonetheless they demonstrated proof-of-concept for future research in thin-film CuInSe<sub>2</sub> devices for lower cost cells. Grindle et al. at the University of Maine were able to make 5% efficient cells [5] by thermally evaporating CuInSe<sub>2</sub> on low-cost substrates. This was followed by the successful work done by Mickelsen and Chen at Boeing Aerospace which was supported by U.S. DOE funding through the Solar Energy Research Institute (SERI). Boeing was able to make 10% efficient CuInSe<sub>2</sub> cells by coevaporation by 1982 [6].

Several groups followed the pioneering work of Boeing. Among those who initiated research programs were ARCO Solar, Institute of Energy Conversion (University of Delaware), and the Solar Energy Research Institute. All these groups were able to quickly reproduce the Boeing results in solar cell efficiency by making cells in excess of 10% [7,8]. Innovative device design (Fig. 2) first proposed by Choudary et al. [9] and reduced to practice by Potter et al. enhanced the blue response of these CuInSe<sub>2</sub> devices and improved the cell efficiency to 12.5% [10]. Further additions of small quantities of Ga (<10%) improved the reported cell efficiency to 14.1% (active area) for 3.5 cm<sup>2</sup> area

device. Boeing also improved the cell performance to 12.9% (active area) for a 1 cm<sup>2</sup> device by the addition of 27% Ga in the CuGaInSe<sub>2</sub> cells [11]. The V<sub>oc</sub> of this device was 555 mV, and was considered a significant improvement.

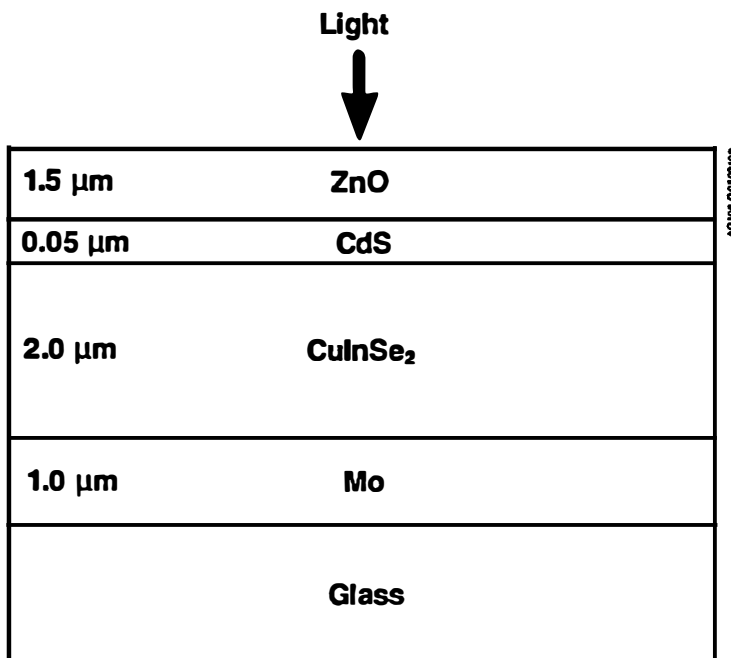


Figure 2 Device structure of a Glass/Mo/CuInSe<sub>2</sub>/CdS/ZnO polycrystalline thin film solar cell

International Solar Electric Technology (ISET), a spin-off from ARCO Solar, was also successful in making 10.9% (active area) devices by a low-cost two-stage process [12]. Mo coated on glass is used as a substrate, on which Cu and then In are deposited by E-beam. The Cu-In sandwich is thermally reacted with H<sub>2</sub>Se gas, forming high quality CuInSe<sub>2</sub>. To complete the cell fabrication, a thin layer of dip-coated CdS is deposited on the CuInSe<sub>2</sub> to form the heterojunction. Using a similar approach, the Institute of Energy Conversion has demonstrated J<sub>sc</sub> of 42 mA/cm<sup>2</sup> [13].

During the 1980s, ARCO Solar developed proprietary processes for manufacturing CuInSe<sub>2</sub> modules using a potentially low-cost approach [14,15]. This success in the manufacturability was a significant step for the CuInSe<sub>2</sub> technology and subsequently led to ARCO Solar's scale-up of large-area modules.

Ermer and co-workers reported on the major advances of the performance of large-area CuInSe<sub>2</sub> modules [16]. They reported achieving an 11.1% efficient 1000 cm<sup>2</sup> module, the most efficient at its size among the various thin films. For even larger areas of about 4000 cm<sup>2</sup>, efficiency in excess of 9% with a power output of 35.8 watts (Fig. 3) for unencapsulated modules was also reported. These modules have now been tested at SERI under natural sunlight for 240 days under both load and open-circuit conditions and have been found to be very stable [17].

### CADMIUM TELLURIDE

Cadmium telluride (CdTe), normally referred to as the "dark horse" of thin film solar cells, has shown improved performance in the past few years. Based on a bandgap of 1.45 eV, which is an optimum match with the solar spectrum, practical CdTe devices could potentially achieve efficiency up to 18%. Theoretical efficiencies are as high as 27.5% [18%].

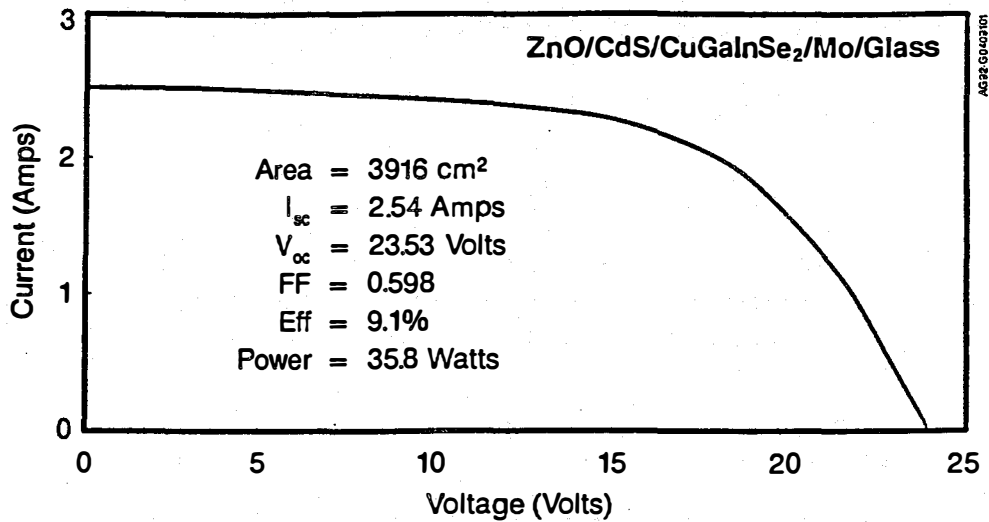


Figure 3 Light I-V characteristics of a large-area 3916 cm<sup>2</sup> polycrystalline thin film CuInSe<sub>2</sub> module

One of the key problems encountered in fabricating thin-film CdTe devices is its contact stability. To circumvent this problem, a research group at Ametek has developed a novel n-i-p cell design, which is shown in Fig.4. The undoped CdTe acts as an intrinsic layer sandwiched between the n-type CdS and p-type ZnTe layers that induce a drift field across the CdTe. Figure 5 shows the Auger depth profile for this cell structure. One of the key processing steps is a heat-treatment at 400°C for about 20 minutes. This step causes significant change in the morphology [19,20] and is the key to high process yields. During the heat treatment, the polycrystalline grains at the CdS-CdTe interface are believed to coalesce or fuse, thus greatly reducing the density of grain boundary states. Recrystallization occurs over the entire thickness of the CdTe film. Using this cell design, Ametek has fabricated 11% cells by electrodeposition [21]. Ametek has also tested their cells and submodules and have reported stability of their devices for 3000 hours.

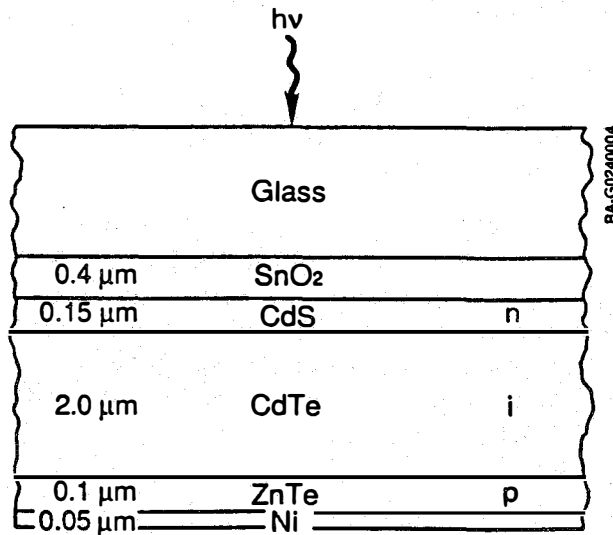


Figure 4 Device structure of a n-i-p n-CdS/i-CdTe/p-ZnTe polycrystalline thin film CdTe solar cell

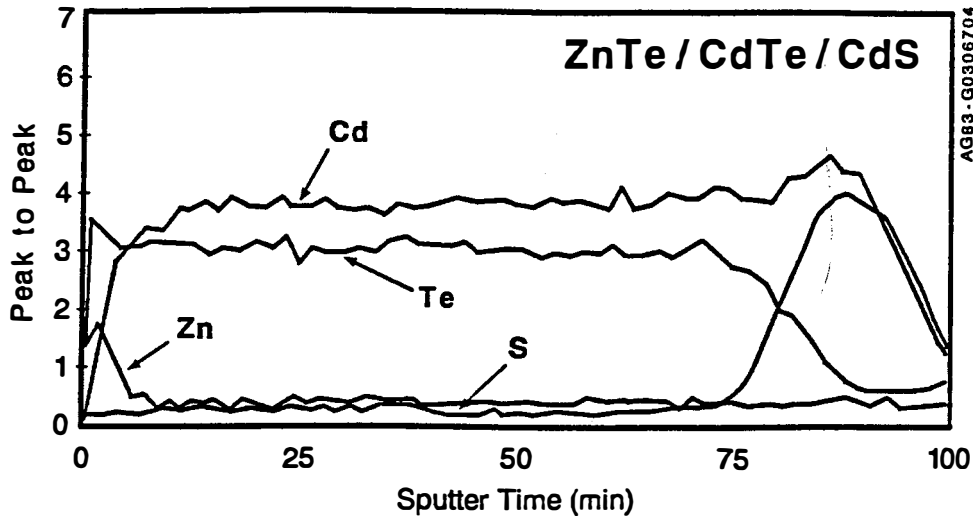


Figure 5 Auger depth profile of a n-i-p n-CdS/i-CdTe/p-ZnTe polycrystalline thin film solar cell

Photon Energy is another successful CdTe group. Their primary focus of research is to fabricate thin film CdTe solar power modules by a potentially low-cost spraying method. To date they have achieved 12.3% efficient small area cells, and 7.3% efficient square-foot module [22]. They have also made prototype four-square-foot CdTe modules for production.

### SERI IN HOUSE RESEARCH

Active investigation is underway at the Solar Energy Research Institute to study the materials growth, characterization and device fabrication of thin film  $\text{CuInSe}_2$  and related alloy materials. SERI makes state-of-the-art  $\text{CuInSe}_2$  devices [23]. Also, extensive support is given to the photovoltaic industry in terms of material characterization such as Auger Electron Spectroscopy, Electron Beam Induced Current, Electron Spectroscopy for Chemical Analysis, Photoluminescence, Scanning Electron Microscopy, Secondary Ion Mass Spectroscopy, Spectroscopic Scanning Tunneling Microscopy, Wavelength Dispersive Spectroscopy, defect chemistry, chemical and heat treatments, stability testing, etc.

### CONCLUSIONS

Polycrystalline thin-film  $\text{CuInSe}_2$  and CdTe solar cells and modules have made rapid advances and are now the leading thin films for PV in terms of efficiency and stability. They have attained the highest cell efficiencies (14.1% for  $\text{CuInSe}_2$  and 12.3% for CdTe), the highest module efficiencies (11.1% for  $\text{CuInSe}_2$  and 7.3% for CdTe on a square-foot; 9.1% for 4 square feet for  $\text{CuInSe}_2$ ); the best stabilities ( $\text{CuInSe}_2$  240 days without degradation), are made by the lowest cost processes (spraying, electrodeposition, sputtering and selenization). The U.S. Department of Energy has increased its funding through an initiative through the Solar Energy Research Institute in  $\text{CuInSe}_2$  and CdTe with subcontracts to start in Spring 1990. The level of federal support for  $\text{CuInSe}_2$  and CdTe is doubling to about \$2.4M for each material. Both  $\text{CuInSe}_2$  and CdTe are now moving out of the lab and into demonstration projects through the Photovoltaics for Utility Sale Applications (PVUSA) proposals. 20 kW systems of  $\text{CuInSe}_2$  supplied by ARCO Solar and 20 KW of CdTe supplied by Photon Energy will be installed in Davis, California, next year for field testing and evaluation.

## ACKNOWLEDGMENTS

The authors would like to thank Amy Swartzlander for doing the Auger depth profile analysis. This work was supported by the U.S. Department of Energy under contract # DE-AC02-83CH10093.

## REFERENCES

1. Five Year Research Plan, 1987-1991, National Photovoltaic Program, U. S. Department of Energy, DOE/CH10093-7, May 1987
2. H.S. Ullal (Ed.), Proceedings of the Polycrystalline Thin Film Program Meeting, Lakewood, CO, August 16-17, 1989; SERI/CP-211-3550
3. K. Zweibel and H.S. Ullal, in Proceedings of the 24th Intersociety Energy Conversion Engineering Conference, Washington, D.C., August 6-11, 1989, pp. 765
4. S. Wagner, J.L. Shay, P. Migliorato, and H.M. Kasper, Appl. Phys. Letts., 25 , 434 (1974)
5. S.P. Grindle, A.H. Clark, S. Rezaie-Serej, E. Falconer, J. McNeily, L.L. Kazmerski, J. Appl. Phys. 51, 5464 (1980)
6. R.A. Mickelsen and W.S. Chen, in Proceedings of the 16th IEEE PV Specialists Conference, San Diego, CA, September 27-30, 1982, pp. 781
7. J.D. Meakin, SPIE Photovoltaics, 543, 1985, pp. 108
8. K. Zweibel and T. Surek, in Proceedings of the 20th Intersociety Energy Conversion Engineering Conference, Miami Beach, FL, August 18-23, 1985, pp. 3398
9. U.V. Choudary, Y.H. Shing, R.R. Potter, J.H. Ermer, and V.K. Kapur, U.S. Patent # 4,611,091, September 9, 1986
10. R.R. Potter, C. Eberspacher, and L.B. Fabick, in Proceedings of the 18th IEEE PV Specialists Conference, Las Vegas, NV, October 21-25, 1985, pp. 1659
11. W.E. Devaney, W.S. Chen, J.M. Stewart, and R.A. Mickelsen, IEEE Trans. on Electron Devices, February 1990, to be published
12. B.M. Basol, V.K. Kapur, and R.C. Kullberg, Solar Cells, to be published
13. R. W. Birkmire, B.E. McCandless, W.N. Shafarman, and R.D. Varrin Jr., in Proceedings of the 9th E.C. Photovoltaic Solar Energy Conference, Freiburg, F.R. Germany, September 25-29, 1989, pp. 134
14. R.B. Love and U.V. Choudary, U.S. Patent # 4,465,575, August 14, 1984
15. J.H. Ermer and R.B. Love, U.S. Patent # 4,798,660, January 17, 1989
16. J. Ermer, C. Fredric, K. Pauls, D. Pier, K. Mitchell, and C. Eberspacher, in Proceedings of the 4th International Photovoltaic Science and Engineering Conference, Sydney, Australia, February 14-17, 1989, pp. 475
17. L. Mrig and S. Rummel, in Outdoor Stability Performance of CIS and CdTe Photovoltaic Modules at SERI, edited by H.S. Ullal, Proceedings of the Polycrystalline Thin Film Program Meeting, Lakewood, CO, August 16-17, 1989, SERI/CP-211-3550
18. J.R. Sites, in Proceedings of the 20th IEEE PV Specialists Conference, Las Vegas, September 26-30, 1988, pp. 1604
19. H.S. Ullal, Electronic Structure of Electrodeposited Thin Film CdTe Solar Cells, May 1988, SERI/TP-211-3361
20. K. Zweibel, H.S. Ullal, and R.L. Mitchell, in Proceedings of the 20th IEEE PV Specialists Conference, Las Vegas, NV, September 26-30, 1988, pp. 1469
21. P.V. Meyers and C.H. Liu, in Proceedings of the 8th E.C. Photovoltaic Solar Energy Conference, Florence, Italy, May 9-13, 1988, pp. 1588
22. S.P. Albright, B. Ackerman, and J.F. Jordan, in IEEE Trans. on Electron Devices, February 1990, to be published
23. R. Noufi and J. Tuttle, in Proceedings of the 9th E.C. Photovoltaic Solar Energy Conference, Freiburg, F.R. Germany, September 25-29, 1989, pp. 283