

SERI/TP-211-2048

UC Category: 63

DE83012131

Progress in Polycrystalline Thin-Film Solar Cells

Kenneth Zweibel

Allen Hermann

Richard Mitchell

July 1983

To be presented at the Solar
World Congress of ISES
Perth, Western Australia
August 1983

Prepared under Task No. 1485.10

WPA No. 425

Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard

Golden, Colorado 80401

Prepared for the

U.S. Department of Energy

Contract No. EG-77-C-01-4042

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 \$4.50
Printed Copy \$7.00

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or 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.

PROGRESS IN POLYCRYSTALLINE THIN-FILM SOLAR CELLS

Kenneth Zweibel, Allen Hermann, and Richard Mitchell

Solar Electric Conversion Research Division
 Solar Energy Research Institute
 1617 Cole Boulevard
 Golden, Colorado 80401

ABSTRACT

Photovoltaic devices based on several polycrystalline thin-film materials have reached near and above 10% sunlight-to-electricity conversion efficiencies. This paper examines the various polycrystalline thin-film PV materials including CuInSe_2 and CdTe in terms of their material properties, fabrication techniques, problems, and potentials.

KEYWORDS

CuInSe_2 , CdTe , CdS , GaAs , Zn_3P_2 , Cu_2Se , Solar Energy Research Institute, polycrystalline thin-film solar cells.

INTRODUCTION

This paper presents recent results of the United States Department of Energy Polycrystalline Thin Film Photovoltaic Program, managed by the Solar Energy Research Institute (SERI). At present, the thin-film devices represented in Table 1 are being investigated.

TABLE 1. Best Reported Efficiencies of Polycrystalline Thin-Film Heterojunction Devices

Material (window/absorber)	Absorber bandgap (eV)	Best Efficiency	Area	Comments
$n\text{-(Cd,Zn)S/p-CuInSe}_2$	1.0	11%*	1 cm ²	Simulated AM1 solar spectrum, ELH lamp at 25°C (Boeing)
$n\text{-(Cd,Zn)S/p-Cu}_2\text{S}$	1.2	10.2%	1 cm ²	Cu_2S formed by ion exchange (IEC)
$pn\text{-GaAs}$	1.4	9%	1 cm ²	$p^+/n/n^+$ all-GaAs homojunction (SMU)
$n\text{-TiO}_2/p\text{-CdTe}$	1.5	7.3%	1 cm ²	CVD deposition (SMU)
$n\text{-CdS/p-Cu}_2\text{Se}$	1.2	5.4%	1 cm ²	Boeing
$\text{Mg/Zn}_3\text{P}_2$	1.5	4.3%	1 cm ²	Schottky barrier (IEC)

* A similar cell, tested at SERI under standard conditions using a xenon solar simulator, produced 10.3% and 10.5% efficiencies at 28°C and 25°C respectively.

PV MATERIALS

CuInSe₂. The 11% CuInSe₂ PV cell developed and reported by Boeing under SERI subcontract is the highest-efficiency thin-film non-single-crystal solar cell. Efficiencies of 10% are commonly reported in the laboratory. Boeing has begun (Sept. 1982) a commercialization joint-venture (Sovolco) with Reading and Bates to commercialize their cells. Sovolco has had preliminary success, depositing high-efficiency cells on low-cost substrates.

One of CuInSe₂'s most important characteristics is its absorption coefficient, the highest among the known PV materials. Kazmerski et al. (1983) measured it in excess of $6 \times 10^3/\text{cm}$ at near-bandgap (1 eV) energies. This absorption coefficient is advantageous because (1) very little thickness (a few tenths of a micron) is needed to absorb the sunlight; and (2) most light is absorbed in or very near the junction field (minority carrier diffusion lengths need not be very great for successful carrier collection). CuInSe₂ cells have demonstrated the highest current density of any solar cells, reaching nearly 40 mA/cm².

CuInSe₂ has demonstrated excellent stability. No degradation has been reported in cells subjected to constant AM1 illumination for 7500 hours at temperatures up to 80°C (preliminary studies on three unencapsulated cells in Seattle air). Some performance degradation has occurred (1) when cells were mechanically damaged during test contacting and (2) at higher temperature and moisture when grid-degradation occurs. Early work on the fundamental properties of CuInSe₂ has been done by Jaffe and Zunger (1983). They called particular attention to unique stability in CuInSe₂ (and other Cu-ternaries) due to the strength of the Cu bonding. This is particularly heartening because the movement of Cu atoms in binary semiconductors (e.g., Cu₂S, Cu₂Se) has led to instabilities such as the formation of Cu nodules that short-circuit the cells. The apparently fundamental stability of Cu-ternaries, suggested by Jaffe and Zunger, gives credibility to ternary rather than binary compounds despite otherwise greater complexity.

The highest-efficiency CuInSe₂ devices are now deposited at Boeing. Boeing's vacuum-evaporated cell (Fig. 1) is a thin-film polycrystalline heterojunction with a CuInSe₂ absorber and a large-bandgap (2.4 eV) (CdZn)S window. The CuInSe₂ layer is deposited with non-constant compositions (Table 2), but mixing takes place during deposition. The final cell layer compositions and electronic properties are under close study (Figure 2). Figure 2 suggests that the layers in the final CuInSe₂ cell are homogeneous within one atomic-percent measurement error. However, sub-atomic-percent inhomogeneities (if they exist) could be responsible for significant variations in layer electronic properties. The bilayer deposition technique appears to produce more efficient cells. Sub-atomic-percent electronic properties may account for the need for a bilayer deposition: Carrier concentrations and conductivity type change very rapidly at near-stoichiometric compositions.

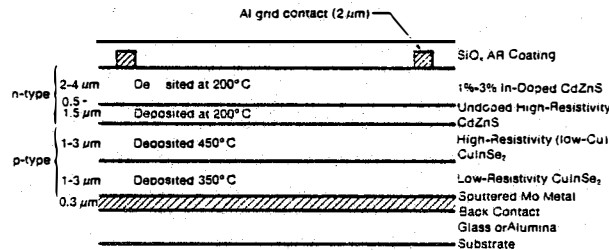


Fig. 1. The Boeing CdZnS/CuInSe₂ cell, showing deposition temperatures, film thicknesses, and compositions of the layers during deposition.

TABLE 2. EDAX-Measured Compositions of CuInSe_2 Diagnostic Side-Strio Layers Formed during the Deposition of Mixed-Layer Cells*

Sample ID	Layer	Composition (Atomic Percent)		
		Copper	Indium	Selenium
A	1	26.5	24.0	49.5
	1 + 2	25.1	26.3	48.6
	2	19.3	29.1	51.6
B	1	26.2	24.8	49.0
	1 + 2	24.8	26.5	48.9
	2	20.0	23.0	52.0
C	1	25.6	26.6	47.8
	1 + 2	23.7	27.6	48.7
	2	20.7	28.7	50.6

*Note: Layer 1 (nearly stoichiometric, with Cu excess) is deposited first, directly on the substrate; layer 1 + 2 is a transition layer; layer 2 is deposited last, with a Cu deficiency. These values indicate rates of deposition; presently, it is thought that the layers mix during deposition, producing a very nearly stoichiometric, homogeneous film of CuInSe_2 .

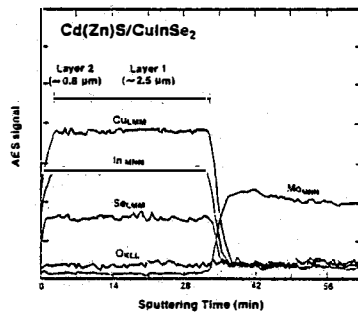


Fig. 2. Composition of Boeing CuInSe_2 film (SERI).

The Cu, In, and Se concentrations do not vary significantly from 25%, 25%, 50% (within 0.5 atomic % measurement error) over the thickness of the film, showing that the layer homogenizes during deposition.

The Boeing vacuum coevaporation is now the most successful deposition technique, but other techniques are being developed. Their aim is to make high-quality films with techniques that are potentially scalable to large areas and high throughput, and hence are potentially low cost.

The Boeing (Hsiao et al., 1983) system for making thin-film CuInSe_2 is a three-source coevaporation from open boats containing the elements. Compositional control is by electron impact emission spectroscopy (EIES), which monitors atoms of Cu and In in the evaporation beam and provides feedback to control the evaporation boat temperatures. The Se rate is measured by a quartz crystal thickness monitor. The open-boat method may present difficulties during scale-up to large areas. A variation on the evaporation technique is the Knudsen cell method being developed by the Institute of Energy Conversion (Birkmire et al., 1983). Researchers at IEC have developed a "feed-forward" stoichiometry control in the CuInSe_2 film deposition. Control is by three Knudsen cells (Fig. 3), which are "closed boats" using small apertures for elemental evaporation. Orifice size and boat temperature are controlled. Once the atomic fluxes are calibrated, one can "dial in" the needed stoichiometry. This type of evaporation system has been used in continuous deposition of CdS for making efficient CdS/ Cu_2S devices. Results to date on CuInSe_2 films made by Knudsen cells are most encouraging. Chalcopyrite films of appropriate stoichiometry have been deposited, and first-generation cells have demonstrated AM1 efficiencies on the order of 7.5%.

A promising, large-area method for making CuInSe_2 is sputtering (Thornton et al., 1983). Telic, which has made the highest-efficiency all-sputtered $\text{Cu}_2\text{S}/\text{CdS}$ cell (about 4%), is studying the reactive-sputtering of CuInSe_2 . Telic reported a small-area, 4%-efficient hybrid $\text{CuInSe}_2/\text{CdS}$ cells (evaporated CdS) with a radial sputtering system. The system has uniformity problems due to the placement of the sources. A multi-station, in-line planar-magnetron reactive-sputtering system is being built for depositing larger areas with greater uniformity. An important aspect of this new magnetron sputtering technique is that the plasma is confined near the target material, minimizing damage from unwanted sputtered atoms, ions, and electrons.

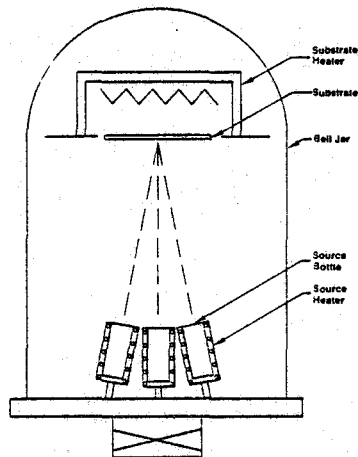


Fig. 3. A schematic diagram (left) of Knudsen cell deposition at IEC.

A close-spaced chemical vapor transport system is being studied at Poly Solar Inc. Rectangular, polycrystalline bulk-CuInSe₂ source material synthesized from the elements is placed adjacent and very near (about 1 mm) a rectangular substrate, and a film is formed by chemical vapor transport using iodine or hydrogen as a transport agent. Films being made early in the program were p-type, with about 10-20 ohm-cm resistivity. Because films are very thin in relation to the bulk source material, many can be made from each source. The entire system can be scaled-up in area if larger-area source material can be synthesized. In initial work with a new window material, ZnO, high V_{oc} over 500 mV has been observed in unstable devices.

An important and as yet not very well understood phenomenon relating to CuInSe₂ is that high-efficiency cells all require post-deposition oxygen heat treatments. Both Boeing and IEC find efficiency enhancements associated with heating completed CdS/CuInSe₂ devices in O₂ at 200°C (Table 3). Work is being done by several groups to understand the effects of the heat treatment on the CuInSe₂ devices.

TABLE 3. Boeing CdS/CuInSe₂ Heat Treatment in Oxygen at 200°C

Cumulative Bake Time	Efficiency (%)	V _{oc} (V)	I _{sc} (mA)	F.F.
Initial (No Bake)	4.19	0.312	32.55	0.412
10 min.	6.77	0.377	35.35	0.509
20 min.	7.20	0.379	35.39	0.537
30 min.	7.33	0.384	35.88	0.536
40 min.	7.54	0.388	35.80	0.546

CdTe. CdTe is a prime PV candidate due to its ideal direct bandgap (nearly 1.5 eV), high optical absorption coefficient (greater than $3 \times 10^4 \text{ cm}^{-1}$ at the band edge energy), and relative ease of deposition. Heterojunction devices based on single-crystal p-CdTe and evaporated CdS reportedly have exhibited efficiencies in excess of 13%, and a privately funded Kodak group has reported a polycrystalline thin-film CdS/CdTe device with 10.9% efficiency (AM2). The CdS and CdTe in this latter case were deposited by close-spaced sublimation. Electrodeposited CdS/CdTe thin-film heterojunction devices have been reported by Ametek, Inc., with about 8% efficiencies and by Monosolar, Inc., with about 9% efficiencies.

The DOE/SERI program has been supporting research in which CdTe is formed by either chemical vapor deposition (CVD) or hot wall vacuum evaporation (HWVE). CVD is a scalable deposition process, and SERI-sponsored research at Southern Methodist University has demonstrated reported 7.25%-efficient TiO₂/CdTe device in which the

CdTe was deposited by CVD and the ITO was ion-beam sputtered. HWVE p-CdTe films have been studied at Stanford University and in-house at SERI. The most recent results from Stanford have shown 4.2%-efficient CdS/CdTe (HWVE) heterojunctions. Schottky-barrier n-CdTe cells with 4% efficiencies have been deposited at SERI. Another major objective in the SERI/DOE program has been to find a way to make an ohmic contact to p-CdTe. One solution is use of an antimony-doped CdTe interlayer incorporated between the p-CdTe and the back contact. Interface resistance has been reduced to about 3.5 ohm-cm² in this method (Chu, 1982).

GaAs. GaAs would be expected to have a great potential as a thin-film polycrystalline material. Single-crystal GaAs devices have attained the highest efficiencies of any solar cell material (22%), and GaAs has proven long-term stability. Unfortunately, polycrystalline GaAs made on low-cost substrates fails to reproduce single-crystal results. The main problem seems to be losses associated with grain boundaries, presumably from shunting effects across the junction. Research at Southern Methodist University is directed to minimizing grain boundary effects by (1) reducing the number of grain boundaries (growing larger grains) and (2) by finding a method to passivate the grain boundaries. Large-area (about 9 cm²) GaAs pn-homojunction devices of nearly 9% efficiency are being made by chemical vapor deposition.

Zinc phosphide has an optimal bandgap (1.5 eV) and can be fabricated from cheap, elements. However, it is difficult to match Zn₃P₂ with a window material to produce a stable, efficient device. Chemical effects at the junction have degraded cell structures with CdS, ZnO, and ITO that had initially good PV performance. The only window material showing stability and some performance is n-ZnSe. ZnSe/Zn₃P₂ devices have had high open-circuit voltages (near 0.8V) but very low currents (about a mA/cm²). The major directions of ongoing research in Zn₃P₂ are to (1) develop low-resistivity n-ZnSe as a heterojunction partner to Zn₃P₂; and (2) to attempt to stabilize the Zn₃P₂ junction with already-developed windows such as CdS, ZnO, or ITO through passivation or incorporation of an interlayer.

Modest progress has been made in the deposition of Cu_{1-x}Se (x about 0.2) by coevaporation from the elements. Efficiencies exceeding 5% in CdS/Cu_{1-x}Se cells have been reported, and initial stability results for unencapsulated cells show only slight degradation (8% relative loss in efficiency after 1500 hours of testing under V_{OC} and simulated AM1 illumination). Continued progress depends in part on successful removal of the Cu nodules that tend to form in the Cu_{1-x}Se films.

ACKNOWLEDGEMENT

This work was supported under DOE Contract No. EG-77-CO1-4042.

REFERENCES

- Birkmire, R.W., Hall, R.B., Phillips, J.E., Meakin, J.D. (1983). Development of Stable, High-Efficiency Polycrystalline Thin-Film Solar Cells Based on CuInSe₂ (Semi-Annual Report). Institute of Energy Conversion, Newark, Delaware.
- Chu, T.L. (1982). Thin-Film CdTe and Zn₃P₂ Solar Cells (Annual Report). Southern Methodist University, Dallas, TX.
- Hsiao, Y.R., Chen, W.S., Micklesen, R.A., Stewart, J.M., Lowe, V., Olsen, L.C., Rothwarf, A. (1983). CuInSe₂/CdSe Thin-Film Solar Cell Development (May 1982-May 1983). Boeing Aerospace Company, Seattle.
- Jaffe, J.E. and Zunger, A. (March 1983). Electronic Structure of CaAlS₂, CuGaS₂, CuInSe₂, CuAlSe₂, CuGaSe₂, and CuInSe₂ (submitted to Phys. Rev. B).
- Kazmerski, L.L., Hallerdt, M., Ireland, C.J., Micklesen, R.A., Chen, W.S. (1983). Optical Properties and Grain Boundary Effects in CuInSe₂, *J. Vac. Sci. Tech.* (in press).
- Thornton, John A., Cornog, David G., Meakin, John D. (1983). Heterojunction Cell Research by Sputter Deposition. Telic Corporation, Santa Monica, CA.