CADMIUM SULFIDE/COPPER SULFIDE HETEROJUNCTION CELL RESEARCH

Critical Studies in Materials and Durability

Quarterly Progress Report

July 1 - September 30, 1979

MASTER

XS-9-8310-1

November 1979

Institute of Energy Conversion
University of Delaware
Newark, Delaware 19711

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use or the results of such use of any information apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

Supported by the Solar Energy Research Institute, Report No. XS-9-8310-1-01

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

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.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

1. ABSTRACT

Quantitative studies of the structure of CdS and (CdZn)S films have been initiated. The influence of deposition conditions on grain size and morphology has been established. Some information on the distribution of defects and impurity clusters in deposited CdS films has been obtained using transmission electron microscopy. Cu_2S films removed from CdS/ Cu_2S cells have been examined using both the scanning and transmission electron microscopy. Structural differences resulting from the method of Cu_2S preparation have been identified. Basic studies designed to reveal the ultimate life limiting mechanisms in CdS/ Cu_2S cells has been initiated. Equipment has been built for studying the optical and electronic changes which occur in Cu_2S during oxidation and reduction cycles. A test set up has been assembled for maintaining cells in various ambients while exposed to sunlight. An analysis of the influence of copper diffusion into the CdS has been initiated.

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any of its 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.

2. Table of Contents

	<u>Page</u>
1. Abstract	1
2. Table of Contents	2
List of Illustrations	3
3. Introduction	5
4. Task E1. Structural and Materials Analysis	7
4.1 Phase E1.1. Structure Preparation CdS, (CdZn)S	21
4.2 Phase E1.2. Influence of Heat Treatments CdS, (CdZn)S	32
4.3 Phase E1.3. Impurity and Copper Diffusion Effects	32
4.4 Phase E1.4. Defect and Grain Structure Cu ₂ S	33
5. Task E2. Cell Durability	46
5.1 Phase E2.1. Controlled Oxidation-Reduction Cu ₂ S	47
5.2 Phase E2.2. Cell Response to Oxidation	52
5.3 Phase E2.3. Life Test Cells	52
5.4 Phase E2.4. Interdiffusion and Cell Integrity	57
5.5 Phase E2.5. Illumination and Voltage Stress Tests	61
5.6 Phase E2.6 Multiple Stress Tests	61
6. Future Developments	62
7. References	63

LIST OF ILLUSTRATIONS.

- Figure 1 Transmission electron micrographs from the center of CdS film #638.
- Figure 2 Transmission electron micrograph of CdS #638 from close to the copper substrate/CdS interface.
- Figure 3 Centered dark field image showing fine grains at back surface of CdS layer. Smallest spots are grains ~ 10 nm in diameter at the back surface, larger spots are grains 30-50 nm in diameter, probably lying just above the back surface.
- Figure 4 Transmission electron micrographs of the same region of the center of a CdS #638 film showing (a) dislocations A visible and (b) invisible, under the reflections shown.
- Figure 5 Fringe images in a transmission electron micrograph of CdS #638 from the center of the film (centered dark field $[10\bar{1}0]$ reflection).
- Figure 6 Transmission electron micrographs showing (a) a typical region of CdS #685 with X-ray spectrum (lower left) from region outlined in white, (b) a region of the same specimen ~ 20 μm from that in (a) showing Si and Cl in the spectrum (lower left) from the region outlined. Lower center shows the spectrum produced by subtracting the CdS spectrum in (a) from that in (b). Upper left shows selected area diffraction pattern from fine grained region in upper right of main picture.
- Figure 7 A schematic diagram describing the main features of the CdS deposit.
- Figure 8 Three dimensional schematic of the grain structure of a vapor deposited CdS film.
- Figure 9 SEM micrograph showing the grain boundary grooving after stripping the Cu_2S surface layer. Marker = 1 μm
- Figure 10 Surface topography and grain structure of CdS films deposited at a substrate temperature of 195°C at the indicated rates. Tilt 20° perpendicular to micron marker.
- Figure 11 Surface topography and grain structure of CdS films deposited at a substrate temperature of 230°C at the indicated rates. Tilt 20° perpendicular to micron marker.
- Figure 12 Surface topography and grain structure of $(\text{CdZn})\text{S}$ films deposited at a substrate temperature of 195°C at the indicated rates. Tilt 20° perpendicular to micron marker.

- Figure 13 Surface topography and grain structure of (CdZn)S films deposited at a substrate temperature of 230°C at the indicated rates. Tilt 20° perpendicular to micron marker.
- Figure 14 Variation of the observed grain size for CdS and (CdZn)S films as a function of deposition rate and substrate temperature.
- Figure 15 SEM micrograph of a Cu₂S layer stripped from a CdS/Cu₂S cell produced by the solid state reaction.
- Figure 16 (a) Dark field TEM micrograph of Cu₂S.
(b) Dark field TEM micrograph showing dislocations in the Cu₂S layer.
- Figure 17 (a) SEM micrograph of Cu₂S stripped from CdS/Cu₂S cell made by solution reaction.
(b) Cu₂S layer showing long spikes.
- Figure 18 (a) TEM micrograph of Cu₂S film stripped from solution reaction CdS/Cu₂S cell. Cell # 685 A2-1.
(b) TEM micrograph of Cu₂S film stripped from solution reaction CdS/Cu₂S cell. Cell # 778 B1-4
- Figure 19 (a) SEM micrograph of stripped Cu₂S layer from cell # 685 A2-1. Only wall intrusions visible.
(b) SEM micrograph of stripped Cu₂S layer from cell # 778 B1-4. Clusters of close spaced intrusions are indicated.
- Figure 20 (a) Deduced structure of the Cu₂S layer produced by solid state reaction on unetched CdS.
(b) Deduced structure of the Cu₂S layer produced by solution reaction on etched CdS.
- Figure 21 Transmittance curves for 1000-2000 Å Cu₂S layers based on Mulder⁽¹⁹⁾ data for n and k.
- Figure 22 Reflectance curves for 1000-2000 Å Cu₂S layers based on Mulder's⁽¹⁹⁾ data for n and k.
- Figure 23 Set up for the in situ measurement of resistivity and absorptance of Cu₂S films.
- Figure 24 Hermetic enclosure for multiple cell testing.
- Figure 25 Gas flow diagram for multiple cell testing.
- Figure 26 Data acquisition system for accelerated and roof top cell testing.
- Figure 27 Copper concentration contours for diffusion into a cylindrical CdS grain.

3. INTRODUCTION

The improvement in energy conversion efficiency and the development of reliable cell production techniques under Subcontract XS-9-8309-1 is heavily dependent on the depth and reliability of the available materials information. Although there is substantial information in the literature on the various component materials, CdS, (CdZn)S and Cu_2S , it has become increasingly clear that information derived from the actual materials comprising specific cells was crucial. The present program is designed to provide such information. Major experimental techniques that will be used include scanning and transmission electron microscopy, X-ray diffraction or fluorescence and a range of optical techniques.

The crystal and grain structure of CdS and (CdZn)S layers for which parallel cell information is available has now been quantified. The relationship between deposition conditions and grain size has been established. Transmission electron microscope (TEM) studies of the CdS layers have revealed a hitherto unsuspected distribution of impurity clusters. It was anticipated that the films would show a high population of dislocations and this has been confirmed. Unanticipated faulting has also been observed. The characterization of as-deposited layers will be followed by studies of the influence of post-deposition heat treatments. Such treatments have been found to improve solar cell performance particularly in the case of the (CdZn)S layers.

The ultimate durability of this type of thin film cell can only be assured as a result of both realistic life testing and the identification and characterization of all relevant degradation modes. A roof top deployment

system has been designed and built and the development of the data acquisition system is now well in hand. A facility which will allow the simultaneous observation of electronic and optical changes in Cu_2S layers during oxidation and reduction is almost complete. Theoretical studies of the influence of copper diffusion into actual rather than idealistic $\text{CdS}/\text{Cu}_2\text{S}$ cell structures has been initiated. Preparatory work for other phases in the durability task are well in hand.

4 Task E1 Structural & Materials Analysis

This section of the program is intended to provide a greatly enlarged fundamental understanding of the structure and properties of the CdS or (CdZn)S and Cu₂S layers. Prior to the initiation of the contract in July 1979, a substantial amount of research had been conducted on the CdS layer. This work is reported here as it represents a valuable contribution to the goals of the program.

Preliminary transmission electron microscope studies were conducted on as-deposited CdS with the aim of characterizing the grain size and internal defect structure. Grain size, shape and orientation from material near the top surface and the center of the deposit consisted largely of grains $\sim 2 \mu\text{m}$ in diameter with occasional larger grains $\sim 10\text{-}15 \mu\text{m}$ in diameter, see Fig. 1. Clearly the grain size is in general much less than the diameter of the pyramids ($\sim 15 \mu\text{m}$) that are characteristic of the top surface of deposited CdS films.⁽¹⁾ The grain size of the CdS $\sim 2 \mu\text{m}$ from the back face was uniform and is $\sim 1 \mu\text{m}$, see Fig. 2, whereas at the back surface it was 10-50 nm, see Fig. 3.

At this point it should be noted that the overall fine mottling of the image is argon ion damage produced during thinning of the electron microscope specimen. It is confined to a layer 10-30 nm deep on the top and bottom surfaces of the thin foil. Ion damage is not expected to alter either the grain size or orientation. Neither should it alter significantly the overall dislocation array. Thin foils of single crystal CdS were entirely dislocation free when produced under identical conditions.

Figure 1 Transmission Electron Micrograph from the Center of CdS Film #638.

1 μm

Figure 2 TEM of CdS Film #638 from close to the Cu/CdS interface.

1 μ m

3000 Å
↔

Figure 3 Centered dark field image showing fine grains at back surface of CdS layer. Smallest spots are grains ~ 10 nm in diameter at the back surface, larger spots are grains 30-50 nm in diameter, probably lying just above the back surface.

Examination of the grain boundaries in detail showed that most were irregular, see for example the arrowed boundaries in Fig. 1. The straight segments of grain boundaries visible in the central and top regions of the CdS film, Fig. 1, implies that certain grain boundary planes may be favored energetically.

Preliminary studies of the growth direction of the CdS grains have been conducted, together with approximate measurements of the misorientations between them. The analysis involved indexing selected area electron diffraction (spot) patterns taken at zero specimen tilt.⁽²⁾ The results showed that, while many grains had growth directions with 5° of (0001) a significant fraction $\sim 30\%$ had orientations $\sim 10^\circ$ from (0001). Deviations of 25° from (0001) were not uncommon. Good statistics are not available at present since only 32 measurements have been made on a total of four specimens. However qualitative analysis of diffraction patterns viewed directly in the microscopy generally confirmed the above estimates.

Consider now the misorientations of the grains about the growth direction. Most were found to be rotated $1-5^\circ$ relative to each other while about 30% were rotated more than $\sim 10^\circ$. Again rotations of 25° were not uncommon. Single diffraction patterns such as these do not provide full information about the misorientations across grain boundaries.⁽²⁾ However they are an approximate indication that they are primarily small angle rather than high angle grain boundaries in the sense defined by Gleiter and Chalmers.⁽³⁾ It must be pointed out that there may be errors ($\sim \pm 3^\circ$) in the determination of grain growth directions due to the bending of the thin foil. Furthermore, more grains must be studied before definite conclusions can be drawn and accurate Kikuchi line analysis⁽²⁾ is to be preferred. Nevertheless, the general trend of the observation is reasonably clear.

The presence of many bend contours in the thin foils reflects the strain in the CdS film⁽⁴⁾ and is not a consequence of mishandling of the sample.

Dislocation Arrays.

Dislocations could clearly be seen in all thin foils except those from the back surface itself. In the latter case the grains were too small to resolve dislocations in conventional images. The approximate dislocation density was 10^9 cm/cm³ and the arrays are of two types.

1. Long straight dislocations parallel to $[1010]$ arrowed in X in Fig. 1.
2. Irregular dislocations in the center of the large grain in Fig. 1.

A detailed study of the Burgers vectors of these dislocations has not yet been undertaken because, to obtain an unambiguous result, computer image matching allowing for the anisotropy of elastic constants and dislocation line directions must be performed.^(5,6) These facilities are not available at present. However an initial attempt to specify Burgers vectors approximately using the "g.b. = 0 invisibility" criterion has been made. Four cases of invisibility consistent with $\underline{b} = \frac{a}{X} \langle 11\bar{2}0 \rangle$ have been obtained for individual dislocations clearly lying in the basal plane. An example is shown arrowed in Fig. 4a and b. However invisibility has not been obtained for the long straight segments such as these at X in Fig. 1 despite the use of a wide range of reflections designed to identify $\underline{b} = \frac{a}{2} \langle 1120 \rangle$, which is the most common Burgers vector in the c.p. hexagonal crystal structure. There are several possible reasons for the absence of invisibility. It could be explained in terms of a $\underline{g.b} \times \underline{u}$ effect,⁽⁷⁾ or elastic anisotropy effects. Alternatively they may be groups of dipoles similar to those found in deformed

Figure 4 Transmission electron micrographs of the same region of the center of a CdS #638 film showing (a) dislocations A visible and (b) invisible, under the reflections shown.

magnesium⁽⁸⁾ which are known to have strong residual images when $\underline{g} \cdot \underline{b} = 0$. If necessary, further studies with more suitable dislocation arrays and operative reflections may be undertaken to clarify this issue.

Limited studies using weak beam images⁽⁷⁾ with medium-high resolution have not shown any evidence of dissociation of dislocations like those in Fig. 1 and into partials.

Planar Defects

There is direct evidence for the presence of stacking fault-like defects on the basal plane of some of the grains with inclined growth directions (see fringe images in Fig. 5). However, because these fringes overlap, it has not been possible to analyze whether they are stacking faults, antiphase domain boundaries or δ boundaries.⁽⁷⁾ It is concluded that these fringe images are more likely to arise from grown-in fundamental crystal defects and may be related to polytypism of the type found in iso-morphous ZnS.⁽⁹⁻¹¹⁾ Alternatively the fringes may reflect the relationship between the wurtzite and sphalerite forms of CdS which are related by a shear on the basal plane.⁽¹¹⁻¹³⁾

Contamination of CdS

Scanning transmission electron microscopy combined with X-ray microanalysis has been used to identify regions of contamination in CdS films. Figures 6 a and b show a typical result. The X-ray spectrum in Fig. 6a which was generated from the region outlined in white is shown in the lower left hand corner. Only cadmium and sulfur were present. (The copper arose from a nearby bar of the copper support grid; not from the CdS film.) In contrast the lower left hand side of Figure 6b shows an

Figure 5 Fringe images in a transmission electron micrograph of CdS #638 from the center of the film (centered dark field $[10\bar{1}0]$ reflection).

0.5 μ m Top Cds

Figure 6b TEM from a region about 20 μm from Figure 6a. The grain structure is much finer and the lower left insert shows x-ray evidence for Si, S, Cl and Cd. The lower center insert shows that subtracting the CdS background reveals more clearly the impurities. The electron diffraction pattern indicates a randomly oriented fine grain structure.

X-ray spectrum from the same specimen but obtained from an ultra-fine grained region outlined in white that was $\sim 20 \mu\text{m}$ away from the region in Figure 6a. In addition to cadmium and sulfur, chlorine and silicon are present. If the spectrum in Fig. 6a was subtracted from that in Fig. 6b, the resultant spectrum in Fig. 6b lower center showed the silicon and chlorine more clearly. In other similar fine grained regions of the same specimen, small amounts ($\sim 5\%$) of magnesium were detected as well as silicon and chlorine. All of the fine grained regions etched more rapidly in the ion beam thinning device. Each fine grained, contaminated region was between 2 and $10 \mu\text{m}$ in diameter. Within each region the grains were always smaller and had a wider range of orientation than the uncontaminated regions of the film. This is illustrated by the complex selected area diffraction pattern shown in the upper left of Figure 6b. Note the reflections arrowed which do not index on the wurtzite CdS crystal structure implying that either a new phase, or a different form of CdS was present in this region.

The overall distribution of contaminated regions was in long parallel rows. In one case, up to $\sim 15\%$ of the thin foil consisted of contaminated regions. However in other specimens $< 5\%$ was found.

Limitation in Accelerating Voltage

Use of higher accelerating voltages (up to 1000 kv) than the normal 100 kv enables thicker films and hence material closer to the actual device to be studied. The maximum thickness that can be used in CdS at 100 kv is approximately $0.4 \mu\text{m}$ whereas at 1000 kv 2-5 μm could be studied. In general, the specimen itself limits useful accelerating voltage because

there is a threshold voltage above which the electrons in the beam can produce point defects in the film by knocking atoms from their sites. As a short term estimate of the feasibility of using high voltage electron microscopy, several specimens have been observed under high beam currents at 120 kv. The results imply that 120-200 kv is probably the limit and that HVEM at 500-1000 kv will not be useful.

Conclusions Drawn From the Transmission Electron Microscopy Studies

The details of the microstructure of CdS are summarized in the schematic diagram in Fig. 7. The major conclusions are as follows:

1. The grain size near the center and top surface of the CdS film is $\sim 2 \mu\text{m}$ with some evidence for a few grains up to 10-15 μm in diameter. At the back surface the grain size is 10-50 nm.
2. Approximately 50% of the grain growth directions are within 5° of [0001] while $\sim 30\%$ are between 10° and 25° from it.
3. Typically the approximate misorientation across grain boundaries are small, $<5^\circ$, but $\sim 30\%$ were in the range 10-25 $^\circ$.
4. There is a high dislocation density $\sim 10^9 \text{ cm/cm}^3$ and planar stacking-fault-like defects are observed.
5. There is clear evidence for regions 2-10 μm in diameter containing significant amounts $\sim 2\text{-}10\%$ Si and Cl. In some cases $\sim 5\%$ Mg is also present.
6. The use of high voltage electron microscopy to view thick sections is seriously limited by electron damage to the CdS.

Figure 7 A schematic diagram of the main features of the CdS deposit deduced from the Transmission Electron Microscopy.

4.1 Phase El.1 The Structure-Preparation Relation of CdS and (CdZn)S Layers

Quantitative analysis of the grain structure of CdS and (CdZn)S films and its relationship to the rate of deposition and to the substrate temperature was completed during this period.

The grain boundaries in these films were revealed by dipping the samples in cuprous chloride solution and then removing the Cu_2S thus formed by KCN attack. Because of the preferential formation of Cu_2S in the grain boundaries, the KCN etching produces grooves in the grain boundaries. A typical grain structure obtained by this method for a CdS film is shown schematically in Fig. 8. This three dimensional view of the grain structure was compiled by analyzing SEM micrographs of polished sections, both top surface and cross-section, and the as-deposited surface. Fig. 9 shows in detail the grain boundary grooving by Cu_2S . Extensive studies during the past year have shown that the appropriate reaction times in CuCl (standard cell processing solution) are six and sixteen seconds respectively for CdS and (CdZn)S. The reaction time in KCN is not critical and is usually around 2 to 5 minutes. Comparison of this method of revealing the grain structure to the HCl vapor etching showed that both methods result in identical structures.

A series of experiments were performed to determine the relationship of the grain structure to the deposition parameters. CdS and (CdZn)S films were grown at two different substrate temperatures (195°C and 230°C) and at growth rates ranging from $0.3 \mu\text{m}/\text{min}$ to $4 \mu\text{m}/\text{min}$. Deposition parameters as well as thicknesses and zinc content of these films are given in Table I.

Figure 8 A Schematic Diagram of the CdS deposit deduced from Scanning Electron Microscopy.

Figure 9 SEM micrograph showing the grain boundary grooving after stripping the Cu_2S surface layer. Marker = 1 μm

Table I
Deposition Parameters, Thicknesses and Zinc Content
of CdS/(CdZn)S Films

	Substrate Temperature (°C)	Average Deposition Rate ($\mu\text{m}/\text{min}$)	Thickness (μm)
		<u>CdS</u>	
	195	.36	23.5
		.64	25.6
		1.07	24.6
		2.04	20.4
		3.02	24.2
	230	.31	23.1
		.62	22.3
		1.11	24.4
		1.88	24.5
		2.82	22.6
		<u>(CdZn)S</u>	
Zinc *			
Content			
.07	195	.30	19.0
.08		.58	23.1
.12		1.05	30.6
.15		1.39	22.3
.15		2.32	20.8
~.15		4.08	24.5
.08	230	.35	17.4
.13		.66	21.3
.11		.97	23.3
.12		1.90	22.1
.15		2.90	20.2

* Atom fraction of cation

The zinc content of the films were determined by EDAX. Data reduction of the X-ray intensities was done by an approximate ZAF method and the resulting zinc contents have a relative precision of around 10%.

For each film the average grain dimension in the plane of the substrate was determined by standard quantitative metallographic techniques using Scanning Electron Microscopy. During this analysis the unpolished, etched surface of the films were examined at 0° tilt. The grain diameter utilized is the linear intercept, ℓ , given by L/N where N is the number of grain boundaries intercepting a line of length L . The total length of grain boundary per unit surface area, ℓ_A , is then given by $\ell_A = \pi/2\ell$. ℓ_A is required when computing the contribution to junction area caused by grain boundary intrusions.

Figures 10 to 13 are micrographs showing the as-deposited surface topography and grain structure of CdS and (CdZn)S prepared at substrate temperatures of 195°C and 230°C . From the micrographs two qualitative conclusions can be drawn as to the rate dependence of the structure of both CdS and (CdZn)S:

1. The as-deposited surface becomes rougher with increasing deposition rate.
2. The grain size, at low deposition rates, shows an extremely pronounced bimodal character. The origin of this is not yet well understood.

There are also clear differences between CdS and (CdZn)S. The bimodal grain size distribution is more common in (CdZn)S films. At the substrate temperature of 195°C this type of grain structure is observed at all rates for mixed sulfide films. Furthermore the surface roughness

Figure 10 CdS film deposited on substrate at 195°C.

Figure 11 CdS Films Deposited on Substrate at 230°C .

Figure 12 (CdZn)S Films Deposited on Substrate at 195°C .

Figure 13 (CdZn)S Films Deposited on Substrate at 230°C.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

observed at high rates is more pronounced in the case of the mixed sulfide films.

The results of the quantitative grain size analysis of these films are summarized in Fig. 14. In this figure each data point represents results from two specimens of the same film. Sufficient grains are counted to result in a standard deviation $\bar{\ell}$ of 0.05 μm . Some uncertainty in the deposition rates arise because the source temperature is 850°C at the start of the deposition and rises to the desired value during the first few minutes of the deposition. This situation results in larger uncertainties in growth rates at the higher values.

Figure 14 shows that the grain size increases with increasing substrate temperature and that for (CdZn)S it is always smaller than for CdS. Somewhat unexpected is that the grain size goes through a maximum as a function of rate. Since in this regime of deposition, the surface diffusion rate is smaller than the rate of arrival of atoms onto the substrate the expected behavior would be a continuous decrease of the grain size with increasing growth rate.

The fundamental mechanisms responsible for the bimodal distribution and the occurrence of a maxima in average grain size have not been identified.

It should be noted that the "boundaries" discussed above are unarguably the sites of rapid attack by cuprous chloride. It is equally certain that many of the sites are CdS grain boundaries. Direct comparison of these SEM results with TEM images from the same film will determine whether all the "boundaries" are indeed grain boundaries and whether all boundaries are revealed by this technique.

Figure 14 Variation of the observed grain size for CdS and (CdZn)S films as a function of deposition rate and substrate temperature.

4.2 Phase E1.2 Influence of Heat Treatment and Ambients on CdS and (CdZn)S

Some experiments have been carried out in the cell development program to reduce the resistivity of (CdZn)S films by annealing in hydrogen. The time temperature matrix for this phase is being developed and will be finalized during the next quarter.

4.3 Phase E1.3 Impurity and Copper Diffusion Effects in CdS and (CdZn)S

This phase is scheduled for initiation during the next quarter. A review of the published data is presently being undertaken.

4.4 Phase E1.4 Quantify Defect and Grain Structures of Cu_xS

Preliminary scanning and transmission electron microscopy studies have been performed on Cu_2S films stripped from the CdS substrate. The technique used involves etching away the CdS with 50% HCl at $\sim 22^\circ\text{C}$ for 3 hours.⁽¹⁴⁾ The materials studied were dry and wet processed, the latter involving material from cells with different V_{oc} and J_{sc} .

Cu_2S Grown by Solid-State Reaction

Fig. 15 shows in detail the active interface of the Cu_2S film viewed from the CdS side of the junction. The depressions reflect the large pyramids on the top surface of the CdS. There are short wall intrusions (arrowed) running along the ridges that correspond to the valleys between pyramids on the CdS surface. The depth of the intrusions is $\leq 1 \mu\text{m}$. The form of the interface is not planar, but appears to be stepped; see for example A. Cracks are present, C, as well as holes, H.

Transmission electron microscopy studies of the films confirmed these features to be present. Although measurements of the grain size and orientation have not been performed, grains $\sim 2 \mu\text{m}$ in diameter, i.e. similar to the CdS have been observed, see Fig. 16a. Dislocations are clearly present, see Fig. 16b. Misorientations between the grains appear to be small, essentially the same as those for the CdS. These results confirm the overall concept of the topotactic growth of Cu_2S on CdS.

Cu_2S Grown by the Solution Method

This material also reflects the pyramids and valleys of the CdS substrate, cf Figs. 17a and 17b. However, well-defined walls $\sim 2 \mu\text{m}$ high

Figure 15 Scanning Electron Micrograph of the Cu_2S Layer from a cell made by the solid state reaction. A marks regions that are terraced. C marks a crack and H a hole in the film. The arrows mark wall intrusions.

2000 Å
↔

2000 Å
↔

Figure 16 Dark Field Transmission Electron Micrographs of the Cu_2S stripped from a) Cell made by the solid state reaction. b) Shows dislocations in the bright grain.

(a)

(b)

Figure 17 Scanning Electron Micrographs of Cu_2S Stripped from a Solution Reaction Cell. (a) $\times 2,500$ (b) $\times 10,000$.

are present, Fig. 17b, that correspond to the intrusions long known to exist in solution-grown material. Unlike the solid state reacted material, these walls are not confined to the valleys between CdS pyramids, but are more generally distributed. It is clear that the intrusion depth is not uniform along its length. Furthermore, the regions between the intrusions are not planar but are scalloped. Individual spikes are also present that penetrate to depths of 6-8 μm , Fig. 17b, as well as short cone intrusions $\sim 2 \mu\text{m}$ deep, Fig. 17a at C. The larger spikes appear to be a result of removal of entire CdS grains during etching while the short spikes correspond to pitting during etching. All of the features described above are consistent with scanning electron microscopy studies of etched CdS before production of the Cu_2S film.

High Resolution Studies

Transmission electron microscopy (TEM) studies of stripped Cu_2S films have confirmed the results described above. However, the TEM studies also revealed that there were variations in the thickness of the film on a micron scale. Figure 18a shows a typical region of an unsupported Cu_xS film. It consisted of thick regions (estimated to be 0.4 μm thick) held together with much thinner regions (white areas) on the order of a few tenths of nanometers thick. The diameters of the thick regions correspond to the fine scale pyramid structure produced during the etching of the CdS prior to Cu_2S production. It was concluded that the Cu_2S forms caps on the top of the small pyramids on the etched CdS.

Transmission electron microscopy studies have also shown that the details of the Cu_2S microphology were different for different films. For example, Fig. 18b shows a well-defined stepped structure in solution processed

Figure 18 (a) TEM micrograph of Cu₂S film stripped from solution reaction CdS/Cu₂S cell. Cell #685 A2-1.

Figure 18 (b) TEM micrograph of Cu_2S film stripped from solution reaction $\text{CdS}/\text{Cu}_2\text{S}$ cell. ²Cell #778 B1-4.

material. In this case, the caps are thinner than those in Fig. 18a. Furthermore, they were larger and more hexagonal, reflecting differences in the etching behavior of the CdS.

Differences in Cu_2S film structure are also illustrated in Fig. 19a and 19b which are low magnification pictures of the same films depicted in Figs. 18a and 18b. Figure 19a showed the presence of well-spaced wall intrusions (arrowed) whereas Fig. 19b contained clusters of closely spaced wall intrusions (arrowed).

Discussion

The preliminary electron microscopy studies lead to a picture of the Cu_2S film and $\text{Cu}_2\text{S}/\text{CdS}$ interface that is illustrated schematically in Fig. 20. Fig. 20a shows the overall topography for solid state reacted material. Wall intrusions, cracks and holes are illustrated, as well as the current tentative picture of the $\text{Cu}_2\text{S}/\text{CdS}$ interface. Fig. 20b shows the solution processed case. The wall intrusions are included, together with small and large cone intrusions, large spike intrusions and the Cu_2S caps. Again the picture of the caps shown is tentative because the details vary from film to film depending upon the etching response of the CdS and other, as yet unidentified parameters.

The differences in Cu_2S microphology observed in the wet processed material would be expected to influence cell performance. For example, as the area of thin Cu_2S increases, the value of J_{sc} would be expected to fall because the thin regions would absorb photons less completely and generate fewer free carriers. Furthermore, during oxidation, the thin regions will be attacked rapidly changing initially from chalcocite to djurleite and finally

(A)

(B)

Figure 19 (a) SEM micrograph of stripped Cu_2S layer from Cell #685 A2-1. Only wall intrusions visible.
(b) SEM micrograph of stripped Cu_2S layer from Cell #778 B1-4.

TENATIVE Cu_xS - CdS MORPHOLOGY, BASED UPON TEM AND SEM STUDIES OF Cu_xS REPLICAS

Figure 20 (a) Deduced structure of the Cu_2S layer produced by solid state reaction on unetched CdS .

TENATIVE Cu_xS - CdS MORPHOLOGY, BASED UPON TEM AND SEM STUDIES OF Cu_xS REPLICAS

Figure 20 (b) Deduced structure of the Cu_2S layer produced by solution reaction on etched CdS .

to Cu_2O . In addition, as the number of intrusion walls increases, the active junction is enlarged leading to a reduction in V_{oc} . The cells made from the materials shown in Figure 5 show a 25% difference in V_{oc} but other effects may be contributing to this such as donor density in the CdS. The overall effect on efficiency of the observed Cu_2S structures is extremely complicated as each major cell parameter, J_{sc} , V_{oc} and FF, will be affected. J_{sc} may, for example, be enhanced because of the beneficial light trapping effects of intrusions.

Conclusions

The major conclusions of the section of the work are as follows:

1. Previous pictures of the active junction were highly idealized. The real case in both wet and dry processed material is much more complicated and the details would be expected to determine key cell parameters which bear on both efficiency and durability.
2. The detailed morphology of the Cu_2S layers depends upon processing parameters and the full interrelationship is not yet clear.

Interpretation of Electron Diffraction Patterns

In studying Cu_2S films, extensive use will be made of transmission and scanning transmission electron microscopy. A major tool in identifying the phases present will be selected area electron diffraction. Inspection of published electron diffraction patterns^(1,15) shows that there are differences for the low chalcocite form of Cu_2S . Both computer generated and experimental patterns for the a^*c^* section of reciprocal space due to Putnis⁽¹⁵⁾ match and are different from those reported for thin films of Cu_2S .

deposited on single crystals of CdS.⁽¹⁾ Putnis has shown^(15,16) that ordering phase transformations can be complex with hitherto unreported intermediate phases present. Consequently, the inconsistencies in the literature are interpreted at present as due to metastable forms of Cu_2S in the case where it is formed as a thin film on a CdS substrate. Such a metastable form can be rationalized in terms of both the thinness of the Cu_2S film and the mismatch strain with the CdS. Further work with deposited thin films of Cu_2S will be required to clarify the nature of the metastable phases.

Because the phase diagram for Cu_2S is complex in the region $\text{Cu}_{1.7-2.0}\text{S}$ standard single crystal patterns have been developed to aid rapid phase identification. The phases included were high and low chalcocite, djurleite and digenite. The patterns were developed using the computer programs of Putnis and McConnell.⁽¹⁷⁾ Patterns for approximately 10 sections in reciprocal space were generated for each phase.

5 Task E2 Cell Durability

This task is designed to identify the fundamental mechanisms controlling the CdS/Cu₂S cell stability and to establish the relevant kinetics.

Progress is reported on the determination of the kinetics of Cu₂S oxidation and reduction, the establishment of a highly automated roof top testing facility and the study of interdiffusion between the Cu₂S and CdS layers.

5.1 Phase E2.1 Controlled Oxidation-Reduction of Cu_2S

During this period the goal for this phase has been:

- To model the changes in optical properties to be expected upon controlled oxidation-reduction of Cu_2S layers on glass substrates.
- To design and construct an experimental system which would measure optical properties and the resistivity of the Cu_2S in situ.

Theoretical Modeling

The most general structure to be expected after oxidation can be precisely defined by the rules of stoichiometry. It generally consists of a glass substrate, a layer of Cu_xS with more than one phase present and a layer of Cu_2O . Assuming uniform oxide formation, one can relate the Cu_2O thickness to the stoichiometry of the sulfide layer by⁽¹⁸⁾

$$x = 2(1 - 1.9 \frac{d_1}{d_2})$$

$$\cancel{x} - x = \cancel{x} - 2.38 \frac{d_1}{d_2}$$

where d_1 is the Cu_2O thickness and d_2 is the initial Cu_2S thickness.

The theoretical modeling consists of calculating the reflectance, R , and transmittance, T , of such a composite structure. Figures 21 and 22 show the reflectance and transmittance results for chalcocite (Cu_2S) layers of various thicknesses on a glass with refractive index $n = 1.5$. The optical constants n and k of chalcocite have been taken from Mulder.¹⁹ An average of n and k for light polarized parallel and perpendicular to the c -axis of

Figure 21 Transmittance curves for 1000-2000 $\text{\AA}$ Cu_2S layers based on Mulder⁽¹⁹⁾ data for n and k .

Figure 22 Reflectance curves for 1000-2000 $\text{\AA}$ Cu_2S layers based on Mulder's ⁽¹⁹⁾ data for n and k .

Cu_2S was used. It can be seen that well-defined features characterize R and T at a given thickness.

The presence of more than one phase in the Cu_2S layer can be modeled in various ways, depending on the size d of the crystallites of the different phases:

- Weighted average of R and T for $d \gg \lambda$
- Weighted average of n and k for $d \gg \lambda$, no dipole-dipole interaction between grains
- Maxwell-Garnett model for $d \gg \lambda$, dipole-dipole interaction

However, it is recognized that the model outlined above may still be too simplistic. First of all, it is assumed that the Cu_2O layer forms uniformly over the Cu_2S . Furthermore, during oxidation/reduction heat treatments, Cu_xS goes through extremely complex solid state phase transformations and therefore it may be rather difficult to ascertain the resulting microstructure.

Experimental Arrangement

The experimental arrangement is shown schematically in Fig. 23. It consists of a vacuum tight dynamic tester which sits on the specimen carriage of the Cary-14 spectrophotometer. Sample mounting in the dynamic tester and the resistive heating element were designed to permit the transmission measurement. Oxidation or reduction atmospheres are provided by the continuous flow of Zero Grade Air or Argon-10% Hydrogen. Optical and resistivity measurements can be made either at the reaction temperatures or at room temperature. In the latter case, the cooling rate can be controlled by the flow rate of water.

Figure 23 Set up for the in situ measurement of resistivity and absorptance of Cu_2S films.

5.2 Phase E2.2 Cell Response to Oxidation-Reduction

This phase is scheduled to start in October

5.3 Phase E2.3 Life Testing (Roof Top) of Completed Cells

During this quarter the test facility and the associated data acquisition system have been designed and completed. The important features of the facility are that it provides the cells with an inert atmosphere and I-V tests under natural sunlight or the Institute simulator are entirely computerized.

Cells are deployed in aluminum enclosures (Figure 24) under flowing high purity argon atmosphere. The gas flow diagram for the system is shown schematically in Figure 25. A three station manifold permits the replacement of empty cylinders without interrupting the gas flow. Since all the gas lines are flexible the packages can be brought indoors for testing under the Institute simulator or for adding/removing cells in a glove box under a protective atmosphere. All cells are kept at their maximum power point by appropriate resistive loads. Packages contain bare and sheet glass encapsulated cells. Sheet glass encapsulation provides added protection especially during transport of representative cells to SERI for independent analysis.

The schematics of the data acquisition system is shown in Fig. 26. Measurement of cell characteristics and data storage are accomplished in three steps:

1. Control signals are sent by the slave micro-computer to the cell selector over the control bus. These signals cause one cell to be electrically connected to the indoor cell I-V tester on the cell bus. The present capability of the cell selector is 30 cells, however, it can easily be expanded as needed.

Figure 24 Hermetic enclosure for multiple cell testing.

Gas Purge System Diagram

Figure 25 Gas flow diagram for multiple cell testing.

IEC Data Acquisition System Rooftop Cell Life Tester

University Computing Center

Figure 26 Data acquisition system for accelerated and roof top cell testing.

2. The slave microcomputer runs a cell I-V test and sends the data to the supervisory microcomputer over the data bus.
3. The data file of tests performed is sent over telephone company 1200 baud leased lines to the central university DEC-10 main-frame time-sharing computer. Here the data is integrated into the Data Base for analysis and storage. It can then be accessed over standard 300 baud dial-up lines.

5.4 Phase E2.4 Interdiffusion and Cell Integrity Under Thermal Stressing

Copper diffusion from Cu_2S into the CdS can be conventionally studied by means of capacitance methods. Two main experimental approaches are the differential capacitance method (Lepley)⁽²⁰⁾ and the measurement of the compensation depth (G.A. Sullivan).⁽²¹⁾ However the first method has a major drawback in that the analysis depth is limited by the maximum measurable capacitance and reverse bias that can be applied before breakdown. Therefore, the compensation depth measurement method was chosen for the present investigation and the initial testing of the experimental arrangement have been completed.

Sullivan's method requires the knowledge of the theoretical depth distribution. In the case of polycrystalline thin films the depth distribution has to be calculated taking into account the role of the grain boundary diffusion. The mathematical formalism of the effect of the grain boundary diffusion was laid down by Whipple.⁽²²⁾ Basically the model is a thin slab of thickness $2a$ having a high diffusivity, sandwiched between two low diffusivity semi-infinite planes. The diffusion equation and the boundary conditions for this system are:

$$D' \nabla^2 c' = \frac{\partial c'}{\partial t} \quad (1)$$

$$D \nabla^2 c = \frac{\partial c}{\partial t} \quad (2)$$

$$c = c_0 \quad z = 0 \quad t > 0 \quad (3)$$

$$c = c_0 \quad x = \pm a \quad z \leq z_1 \quad t > 0 \quad (4)$$

$$c' = c \quad x = \pm a \quad z > 2_1 \quad t > 0 \quad (5)$$

$$D' \frac{\partial c'}{\partial x} = D \frac{\partial c}{\partial x}$$

where c_0 is the solubility limit of copper in CdS and z_1 is defined by

$$c'(z_1, \pm a, t) = c_0 \quad (6)$$

This system of equation can be greatly simplified by making two assumptions:

- 1) If c'_0 is defined as the solubility limit in the grain boundary then $c'_0 \gg c_0$
- 2) $D' \gg D$

The second assumption is widely accepted in grain boundary diffusion studies. The first assumption is also quite reasonable since the notion of the limited solid solubility is valid within the framework of equilibrium thermodynamics. Therefore in a defect region such as grain boundary we can expect much larger solubility if not complete solubility.

Under these assumptions, we can take $z_1 = \infty$ and the boundary conditions (4) and (5) are replaced by:

$$c = c_0 \quad x = \pm a \quad z > 0 \quad t > 0 \quad (7)$$

Physically our assumption means that the grain has a continuous copper source at its lateral surfaces as well. Now the problem can be restated to model the cylindrical grain geometry and the anisotropic diffusion observed in thin films of CdS.

The relevant diffusion equation is:

$$\frac{\partial c}{\partial t} = D_{||} \frac{\partial^2 c}{\partial z^2} + D_{\perp} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) \quad (8)$$

where $D_{||}$ and $D_{\perp}$ are the diffusion coefficients respectively parallel and penpendicular to the c axis. The initial condition and the boundary conditions are:

$$c = 0 \quad t = 0 \quad z \geq 0 \quad 0 \leq r \leq r_0 \quad (9)$$

$$c = c_0 \quad t > 0 \quad z = 0 \quad \text{and } r = r_0 \quad (10)$$

where $2r_0$ is the grain diameter parallel to the film surface.

The solution of equation (8) is:

$$\frac{c}{c_0} = 1 - \operatorname{erf} \left[\frac{z}{2\sqrt{D_{||}t}} \right] \frac{2}{r_0} \sum_{n=1}^{\infty} e^{-D_{\perp} \alpha_n^2 t} \frac{J_0(r \alpha_n)}{\alpha_n J_1(r_0 \alpha_n)} \quad (11)$$

J_0 and J_1 are the Bessel function of the first kind of zero and first order.

α_n 's are the positive roots of $J_0(r_0 \alpha_n) = 0$. The constant concentration contours, obtained from equation (11) are shown schematically in Fig. 27.

It is clear that parallel plate capacitor model is only an approximation.

In the case of $\text{CdS}/\text{Cu}_2\text{S}$ solar cells the equivalent capacitor geometries depends on the Cu_2S formation method:

A. Solution Reaction

This process results in the penetration of Cu_2S thru the grain boundaries to about $1 \mu\text{m}$ depth (see section 4.4). Then the equivalent capacitor is:

Figure 27 Copper concentration contours for diffusion into a cylindrical CdS grain.

B. Solid State Process

In this case the Cu_2S penetration is assumed to be negligible which gives:

5.5 Phase E2.5 Illumination and Voltage Stress Tests

The design of the experimental arrangement which incorporates continuous illumination and protective atmosphere for cells during testing was completed. The facility is in the construction stage.

5.6 Phase E2.6 Multiple Stress Tests

This phase is scheduled to start in January.

6. Future Developments

During the next quarter the influence of heat treatments on the structure of the CdS and (CdZn)S substrates will be carried out. Further work will be carried out on impurity and copper diffusion effects and on the direct examination of Cu_2S layers in the transmission electron microscope.

The set up for controlled oxidation and reduction of the Cu_2S layer is complete and the first experiments will be carried out. Roof top deployment and accelerated testing of cells protected from the atmosphere will be initiated.

7. REFERENCES

1. W. F. Tseng and I. G. Greenfield, Phys. Stat. Sol. (a) 27, 643, 1974.
2. J. W. Edington, "Practical Electron Microscopy in Materials Science," Vol. 2 Electron Diffraction in the Electron Microscope, Pub. MacMillan, 1975.
3. H. Gleiter and B. Chalmers, Progress in Materials Science, Vol. 16, 1972.
4. J. V. Masi, Semi-Annual Progress Report, ILZRO CC-28, June 1979.
5. A. K. Head, P. Humble, L. M. Clarebrough, A. J. Morton and C. T. Forwood, "Computed Electron Micrographs and Defect Identification," Pub. North-Holland, Amsterdam, 1973.
6. P. J. Jones and J. W. Edington, Phil. Mag. 25, 729, 1972; ibid, 27, 393, 1973.
7. J. W. Edington, "Practical Electron Microscopy in Materials Science," Vol. 3 "Interpretation of Transmission Electron Micrographs," Pub. McMillan, 1975.
8. P. B. Hirsch and J. S. Lally, Phil. Mag. 12, 595, 1965.
9. I. T. Steinberger, J. Bardas and Z. H. Kalman, Phil. Mag., 35, 1257, 1977.
10. K. N. Rai, O. N. Srivastava and P. Krishna, Phil. Mag., 21, 1247, 1970.
11. E. Alexander, Z. H. Kalman, S. Marsix and I. T. Steinberger, Phil. Mag., 21, 1237, 1970.
12. P. M. Williams and A. D. Yoffe, Phil. Mag., 25, 247, 1972.
13. F. Secco d'Aragona, P. Delavignette and S. Amelinckx, Phys. Stat. Sol., 14, K115, 1966.
14. J. R. Szedon, F. A. Shirland, W. T. Biter, T. W. O-Keeffe, S. F. Fonash, Cadmium Sulfide/Copper Sulfide Heterojunction Cell Research, Westinghouse Technical Progress Report No. 3 for period April 1 to June 30, 1978, Contract No. EG-77-C-03-1577.
15. A. Putnis, Amer. Mineral, 62, 107, 1977.
16. A. Putnis, Phil. Mag., 34, 1083, 1976.
17. A. Putnis and McConnell, Contrib. Mineral Petrol. 58, pp. 127-136, 1976.
18. B. Baron, A. W. Catalano and E. A. Fagen, 13th IEEE Photovoltaic Specialist Conference pp. 406-411, 1978.

19. B. J. Mulder, Phys. Stat. Sol. (2), 13, p. 82, 1972.
20. B. Lepley et al., LeVide 34, 1, 1979.
21. G. A. Sullivan, Phys. Rev. 184, 184, 1969.
22. R. T. P. Whipple, Phil. Mag. 45, 1225, 1954.