CADMIUM SULFIDE/COPPER SULFIDE HETEROJUNCTION CELL RESEARCH

Critical Studies in Materials and Durability

Quarterly Progress Report No. 2

October 1 - December 31, 1979

XS-9-8310-1

April 1980

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Institute of Energy Conversion
University of Delaware
Newark, Delaware 19711

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1. ABSTRACT

A systematic comparison between the CdS grain size determined by Transmission Electron Microscopy and by Scanning Electron Microscopy of etched surfaces is being carried out. It is found that the etching technique gives a good estimate of the true grain size. Discontinuities in the Cu₂S film produced by solution reaction have been studied by TEM after stripping from the CdS substrate. The various types of Cu₂S intrusions which can arise have been examined using SEM for material produced by the solid state and solution reaction. Large point to point variations in Cu₂S thickness have been observed. Difficulties have been encountered in preparing thin films of Cu₂S on transparent substrates preventing the initiation of direct studies of Cu₂S oxidation kinetics. Towards the end of the reporting period some progress towards a satisfactory Cu₂S film was achieved. An analysis of copper diffusion into the CdS has been carried out, taking into account the actual morphology of the Cu₂S layer on the free surface and the grain boundary penetrations. Cells have been maintained under continuous illumination at open circuit voltage and in one case a high degree of stability has been observed.

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3. INTRODUCTION

The in-depth study of the structure of the various components of the CdS/Cu₂S, (CdZn)S/Cu₂S cells has been continued. Scanning and Transmission Electron Microscopy have been used to reveal in detail the structure of the Cu₂S layer leading to a more acute appreciation of the extreme inhomogeneity of this critical component. Quantitative studies have been made of the rate of grain boundary penetration by Cu₂S during the conventional solution reaction.

A system has been designed and built for maintaining cells under continuous illumination at fixed temperature while protected by flowing high purity inert gas. An automatic bulb replacement system was developed to insure effectively continuous illumination over periods of weeks.

Roof top testing of some cells continued also under flowing gas.

An analysis has been made of the influence of the CdS/Cu₂S junction morphology on the diffusion of copper into the CdS.

4. Task E1 STRUCTURAL AND MATERIAL ANALYSIS

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

TEM studies have been started that are aimed at checking the grain size measurements obtained by the "etching" technique reported in the previous quarterly report.⁽¹⁾

The material studied was CdS substrate #10266 (substrate temperature 195°C, source temperature 968°C, growth rate 0.64 $\mu\text{m}/\text{minute}$, Fig. 10 Ref. (1)). Figures 1a-e show typical individual grains in thin foils that correspond to the center of the CdS film. The largest and smallest grains ($\sim 5 \mu\text{m}$ and $0.75 \mu\text{m}$) are shown in Figs. 1a and 1b. Grain boundaries were frequently irregular as are the grain shapes, see Figure 1c. Many of the grains contained planar defects marked by arrows in Fig. 1d as reported previously.

The average grain diameter was 1.3 μm , determined from the average area of 76 grains assuming a hexagonal grain shape. This value is somewhat less than the value determined by the "etching" technique, 1.8 μm , probably because all grain boundaries are not delineated in the latter technique.

An important issue has been the observation of grain boundaries, using the etching technique with free ends unconnected with other grain boundaries. This has led to speculation that the "etching" technique does not delineate all grain boundaries. Figure 1e is the first observation by TEM of a terminating low angle boundary in CdS (arrowed) which would account for the etching results and help remove uncertainty in the reliability of the etching method.

(a)

(b)

(c)

Figure 1. Dark field transmission electron micrographs of CdS substrate #10266. Marker 1 μm .

(d)

(e)

Figure 1. Dark field transmission electron micrographs of CdS substrate #10266.
Marker 1 μm .

The continuity of the Cu_2S layer produced by the solution reaction has been studied for reaction times of 5, 10, 12, 15 and 20 seconds. The reaction time for routine cell production is 10 seconds. Figures 2a-e show low magnification TEM pictures of typical areas of the stripped Cu_2S films. Clearly the film never becomes continuous with increasing reaction time nor does the thickness become uniform. The large cracks visible in each picture occur at the walls. They may arise either from mismatch strains between the CdS and Cu_2S or slight relaxation of the film during handling. It is unlikely that the Cu_2S film is cracked in situ on the CdS .

4.2 Phase El.2 Influence of Heat Treatments and Ambients on CdS and $(\text{CdZn})\text{S}$

It was found to be possible to reduce the resistivity of $(\text{CdZn})\text{S}$ films by annealing in hydrogen. However control of the deposition conditions under Contract XS-9-8309-1 has succeeded in producing mixed sulfide films of the desired resistivity. It has been concluded that further studies of post deposition heat treatment are unjustified at this time.

4.3 Phase El.3 Impurity and Copper Diffusion Effects in CdS and $(\text{CdZn})\text{S}$

Some related calculations on the diffusion of copper into polycrystalline CdS are given in section 5.4.

4.4 Phase El.4 Quantify Defect and Grain Structure of Cu_2S

A picture has been developed of the details of the $\text{Cu}_2\text{S}/\text{CdS}$ interface in terms of the various types of intrusions that can occur in conventionally processed solution and solid state reacted materials.

1 μm

Figure 2. Transmission Electron Micrographs of Cu_2S stripped from CdS . Solution Reaction Times (a) 5, (b) 10, (c) 12 seconds on substrate 685 M.

(d)

(e)

1 μm

Figure 2. Transmission Electron Micrographs of Cu_2S stripped from CdS . Solution Reaction Times (d) 15, (e) 20 seconds on substrate 685 M.

Solution Processed Material

Intrusions are always present at the bottom of the valleys of the CdS film. These are termed wall intrusions and can penetrate up to $\sim 2 \mu\text{m}$ into the CdS, see Figure 3. Their thickness is $\sim 0.2 \mu\text{m}$ and their separation is $\sim 10\text{-}15 \mu\text{m}$. Walls are the result of the growth of Cu_2S down crevices produced by etching the CdS. The walls may have jagged or smooth tops depending on whether the time of growth is short or long, respectively. The intrusions are the only type of intrusion formed in the high efficiency cells. In less efficient cells, other types of intrusions appear at the heterojunction. The various types of intrusions are illustrated schematically in Figure 4 while examples are shown in Figures 5a-f.

1) Ring intrusions - An example of these intrusions is shown in Figure 5a. They consist of a wall enclosing a region of the Cu_2S film. The walls are thin (less than 100 nm) and the distance between them is approximately $2 \mu\text{m}$. The top of the wall may be smooth or rough. In some cases the walls are not continuous, leading to chisel-shaped spike intrusions. Since the spacing of the walls corresponds approximately to the grain size of the CdS, the ring intrusions are believed to arise from local rapid penetration of the Cu_2S down CdS grain boundaries. The variation of the depth of penetration from boundary to boundary may reflect differences in boundary structure, energy, misorientation, or impurity segregation.

2) Cone intrusions - Cone shaped penetrations of up to $8 \mu\text{m}$ into the CdS have been observed although most are only 2 to $4 \mu\text{m}$ deep. An example is shown in Figure 5b. The intrusions are hollow and arise as a result of Cu_2S growth on the sides of holes produced during etching. In general these intrusions are pointed and can be up to $\sim 2 \mu\text{m}$ in diameter at the base.

Figure 3. SEM Micrograph of Cu_2S film Showing Wall Intrusions in solution processed cell # 778B1-4.

Figure 4. Three dimensional representation of topography of $\text{Cu}_2\text{S}/\text{CdS}$ heterojunction showing different types of Cu_2S intrusions in solution processed solar cells.

(a)

(b)

Figure 5. Scanning Electron Micrographs of Cu_2S intrusion from a $\text{CdS}/\text{Cu}_2\text{S}$ solar cells made by the solution process.
(a) Ring intrusions # 685 M (b) Broken cone intrusion, # 685 M

(c)

(d)

Figure 5. Scanning Electron Micrographs of Cu_2S Intrusions from $(\text{CdZn})\text{S}/\text{Cu}_2\text{S}$ solar cells made by the solution process
 (c) spit intrusion, # 10278.113 (d) Partially formed spit intrusion #10234.211.

(e)

(f)

Figure 5. Scanning Electron Micrographs of Macroscopic Defects in Solar Cells
 (e) Surface of (CdZn)S layer, #M 214 showing loosely bonded spit
 (f) Crack intrusion in CdS/Cu₂S solar cell # 685 M.

3) Spit intrusions - These defects are so named because they are believed to arise from "spits" in the CdS. Spit intrusions consist of large, uneven hollow penetrations of Cu_2S up to $\sim 20 \mu\text{m}$ in width at the base and up to $17 \mu\text{m}$ deep, see Figure 5c. Partially formed spit intrusions are also observed that consist of several pointed curved intrusions and penetrate up to a depth of $\sim 3.5 \mu\text{m}$ and are illustrated in Figure 5d.

Spit intrusions occur when the interface between loosely bonded spits like that in Figure 5e in the CdS is completely or partially etched away. The Cu_2S then forms directly on the surface of the resultant hole or penetrates the crevice at the etched interface.

4) Crack intrusions - These intrusions arise as a result of the growth of Cu_2S down cracks in the CdS film, see Figure 5f. In the worst case, crack intrusions $1.2 \mu\text{m}$ wide and $3 \mu\text{m}$ penetration were observed with a distance between cracks of $\sim 100 \mu\text{m}$.

5) Triple point intrusions - These intrusions sometimes occur where three wall intrusions meet and are Y-shaped at their base. Typically the depth of penetration is greater than $\sim 4 \mu\text{m}$; at least twice that of the wall itself. The tips may be sharp or blunt.

TEM studies of intrusions showed that they were hollow and had similar variations in thickness to the main body of the Cu_2S film. This confirms that they form down crevices and holes produced during the etching step. If these intrusions had formed directly by diffusion down grain boundaries they would be expected to be solid and to have essentially constant thickness.

Solid State Reacted Materials

The details of these films are much simpler than those produced by the solution process. The film is much more uniform, see Figure 6a, and reproduces the topography of the as-grown CdS. Shallow wall intrusions penetrate less than $1\text{ }\mu\text{m}$ into the CdS valley bottoms, see Figure 6b, and the occasional shallow cone intrusions penetrate less than $0.5\text{ }\mu\text{m}$ into the sides of the CdS hills near valley bottoms. The CdS-Cu₂S interface has a terraced structure, see arrow in Figure 6a. The only major defects that develop in the film are cracks and holes, see C and H, Figure 6a. The holes probably arise from unreacted CuCl which is dissolved by the HCl during specimen preparation. Transmission electron microscopy demonstrated that the intrusions were solid and of uniform thickness.

The Influence of Microstructural Features on Cell Performance

Several of the microstructural features described in the previous sections would be expected to influence cell performance. Unfortunately changes in materials production parameters tend to alter more than one aspect of the microstructure. Consequently it is not in general possible to correlate specific changes in individual features with alterations in electrical properties. Nevertheless, it is relevant to consider how various aspects of the microstructure would be expected to influence cell performance. These are discussed below.

Consider first spits in the CdS layer. Those that contain high levels of silicon and chlorine will develop local modifications in the energy band diagram of the heterojunction. This would be expected to increase losses in short circuit current, I_{SC} , and open circuit voltage, V_{OC} .

(a)

(b)

Figure 6. (a) Transmission Electron Micrograph of Cu_2S film stripped from solid state reaction $\text{CdS}/\text{Cu}_2\text{S}$ solar cell #M155A1.4. (b) Scanning Electron Micrograph of Cu_2S from the same cell. H-holes, C-cracks, A-terracing. The arrows indicate shallow wall intrusions.

The influence of intrusions has been considered by several workers.^(2,3,4) Simple considerations lead to the conclusion^(3,4) that cells with intrusions should have reduced V_{OC} and, as the intrusion density increases, V_{OC} will continue to fall. Experimentally it has been found that the appearance of ring intrusions can lead to a reduction in V_{OC} of up to 30 mV. This compares well with the calculated value of 20 mV obtained by substituting junction area measurements from electron micrographs in the relation⁽⁴⁾

$$V_{OC} = + \frac{kT}{q} \ln \frac{J_{sc}}{q N_{c2} s_i} - \frac{kT}{q} \ln \frac{A_j}{A_{\perp}}$$

Where

J_{sc} = short circuit current density

q = electronic charge

s_i = interface recombination velocity

ϕ = activation energy as described elsewhere (4)

N_{c2} = effective density of states in the conduction band of CdS

A_j = junction area

$A_{\perp}$ = planar area

Although V_{OC} falls with increasing intrusion density, I_{sc} would be expected to increase because of the greater opportunity for current generation in the Cu_2S .^(2,3) This arises both from the greater effective thickness of the Cu_2S and because there will be more opportunity for sideways scattered light to enter the Cu_2S and generate an electron current.

Consideration of sharply pointed cone intrusions leads to the conclusion that they may cause V_{OC} to decay with time. This arises because the enhanced electric field at the tips of these intrusions causes tunneling which can produce a high local current density and therefore localized heating. The increase in temperature results in an increase in diode current J_0 and a decrease in V_{OC} .⁽⁵⁾ Another effect of the increase in temperature is that copper vacancies are generated in the Cu_2S and copper is driven out of the Cu_2S .⁽⁶⁾ In confirmation of this theory, nodules up to $\sim 1 \mu m$ in diameter have been observed at the tips of some intrusions of cells that have been exposed to sunlight, see Figure 7. Because the energy barrier between copper and CdS is lower than that between the Cu_2S and CdS, copper migration is accompanied by an increase in diode current J_0 and this causes a further decay in V_{OC} with time. Extensive growth of copper on the tips of deep cone intrusions may eventually lead to shorting of the Cu_2S to the back contact of the cell.

The observed variation in the thickness of the Cu_2S would be expected to lead to regional differences in the density of free carriers. Thick regions will be more active generators than thin regions because they will absorb more light. It is estimated that in some cases up to 20% of the junction area may be in regions of Cu_2S that are less than 50 nm thick. It would be expected that this would lead to a significant lowering of J_{SC} . The occurrence of a terraced heterojunction, such as has been observed in some solution processed and in all solid state reacted material, may enhance the light trapping properties of the interface and hence increase J_{SC} .

Figure 7. Cu_2S stripped from a $(\text{CdZn})\text{S}/\text{Cu}_2\text{S}$ cell #10236-112 after exposure to light showing a nodule at the tip of a cone intrusion.

The existence of thin regions of Cu_2S will increase the susceptibility of the solar cell to trace oxygen. In such regions the development of a monolayer of copper oxide would be enough to drive the stoichiometry from the chalcocite to the djurelite region leading to local reduction in efficiency of light conversion to electricity.⁽⁷⁾

All discontinuities in the Cu_2S film cracks, holes, or gaps between Cu_2S caps would be expected to reduce V_{OC} , J_{SC} and fill factor. Such defects may also cause shorts between the collection grid and the CdS if they are large enough.

The following conclusions may be drawn from the work reported here.

- 1) The grain size, dislocation density, planar defect, silicon and chlorine impurity distribution have all been characterized in CdS. A diagram showing these aspects of the material is shown in Figure 7, Ref. 1.
- 2) Cu_2S films grown by the solution method have been shown to contain wall intrusions that correspond to the bottom of valleys in the CdS. Such films are noncontinuous and have variable thickness on a microscopic scale. The interface between the Cu_2S and the CdS may be smooth or terraced.
- 3) A wide range of intrusions with different morphologies have been shown to occur in Cu_2S films grown by the solution method, if the growth conditions for the CdS film involved are not optimized. Figure 4 shows these schematically.
- 4) Holes and cracks have been identified in solid state reacted Cu_2S films.

5) Defects including holes, cracks, a high intrusion density, sharply pointed intrusions, variations in Cu_2S thickness and continuity, as well as spits in the CdS , may be expected to degrade the performance of a cell to varying degrees.

5. Task E.2 CELL DURABILITY

5.1 Phase E2.1 Controlled Oxidation-Reduction of Cu_2S

During this period efforts were concentrated on preparing thin Cu_2S films on glass substrates (Corning 7059) by completely converting vapor deposited CdS films. Several experiments were performed with different CdS film thicknesses using either solution or solid state reactions with cuprous chloride. In all cases the final Cu_2S film peeled off the glass substrate. During the solution reaction the loss of adhesion took place in the reaction bath. In the case of the solid state reaction the loss of adhesion was observed during the rinsing of cadmium chloride after the reaction. When the initial CdS film was deposited on sand blasted glass the complete conversion was successful and good adhesion of the Cu_2S films was observed. However because of the rough surface of the substrate, these samples are not amenable to optical analysis.

The loss of adhesion showed that the procedure used in cleaning the glass substrates were not adequate. After an extensive review of the literature on surface cleaning techniques^(8,9,10) ammonium bifluoride ($\text{NH}_4\text{F} \cdot \text{HF}$) treatment and baking procedure was adopted. The results obtained with this new procedure will be available in the next reporting period.

5.2 Phase E2.2 Cell Response to Oxidation-Reduction

To study the cell response to oxidation-reduction heat treatments the dynamic tester described previously⁽¹⁾ has been modified to accommodate cells with an inter-digitated grid structure. The experimental arrangements also includes a light source and the necessary electronics to record the I-V

characteristics (both dark and simulated AM1) and to measure the sheet resistance of the Cu_2S layer. With this arrangement cells need not be removed from the heat treatment atmosphere for measurements.

The oxidation heat treatments will be conducted in zero-grade air and the reducing heat treatments in $\text{Ar} + 10\% \text{H}_2$. In parallel with the oxidation-reduction heat treatments on a cell, a similar cell will receive the same heat treatment (time/temperature) in Argon. Argon heat treated cells will permit the decoupling of the oxidation-reduction and diffusion effects.

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

Five cells have been exposed to natural sunlight under a protective flowing Argon atmosphere since 11/8/79. All cells were kept at 0.35 V by resistive loads. The average initial efficiency of the cells was 6.3%. Packages were removed periodically from their exposure site for testing in the Institute's simulator. First such tests were performed after 13 days of exposure and unstable I-V characteristics (hysteresis) along with severe drop in cell performance were observed for all cells. Similar results were obtained for longer exposure times.

It is believed that this high rate of failure is the result of an "infant mortality" probably due to some sort of processing defect. This type of failure was not observed during multiple stress tests (continuous illumination/voltage/temperature) which are described below (Phases E2.5 and E2.6).

A new batch of cells is being prepared to replace the present set of cells.

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

During the previous reporting period, copper diffusion into the polycrystalline CdS films was analyzed theoretically. Assuming cylindrical grains (diameter $2r_0$) and taking into account the grain boundary diffusion, the Cu concentration in each CdS grain is given by⁽¹⁾

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

It is assumed that the normal to the overall diffusion front is parallel to the c axis of the CdS. D_{11} and $D_{\perp}$ are respectively diffusion coefficients parallel and perpendicular to the c axis. c_0 is the solubility limit of Cu in CdS and J_0 and J_1 are the Bessel functions of the first kind of zero and first order. α_n 's are the positive roots of $J_0(r_0) = 0$.

If a $\text{Cu}_2\text{S}/\text{CdS}$ couple is heated for a time t at a temperature T such that $C_0(T) > N_D$ (N_D : carrier density in CdS) a compensated region will form. In principle, dark, zero bias capacitance measurement will determine the geometry of this compensated region and thus permit the determination of the diffusion coefficients $D_{\perp}$ and D_{11} .

a) Capacitance due to the Compensated Region - The capacitance of the compensated region is different for Cu_2S formed by the solution reaction or the solid state reaction. In the case of solution reaction the geometry for a single CdS grain is shown in Figure 8.

In this case we have a planar capacitance in parallel with a cylindrical capacitance

$$C = \frac{\epsilon_0}{a} (r_0 - b)^2 \pi + \frac{2\pi\epsilon_0 (1-a)}{\ln \frac{r_0}{r_0-b}} \quad (2)$$

Figure 8. Equivalent Capacitance Model for a Single Grain.

Here l is the grain boundary penetration depth of Cu_2S and a and b the compensation depth from the free surface and grain boundary respectively. Equation (2) assumes that the $C = N_D$ contour is perfectly cylindrical. The validity of which will be examined in Section d. For a polycrystalline sample of area A and average grain diameter $2r_0$, it can be shown that

$$\frac{c}{A\epsilon_0} = \frac{\beta}{a} + 6.5 L_A^2 \frac{a-R}{l_n B} \quad (3)$$

where $\beta = \left(\frac{r_0-b}{r_0}\right)^2$ and $L_A = \frac{\pi}{4r_0}$, the grain boundary length per unit area of surface.

For the case of Cu_2S formed by the solid state reaction, there is no cylindrical capacitor and equation (3) reduces to

$$\frac{c}{A\epsilon_0} = \frac{\beta}{a} \quad (4)$$

b) Experimental Determination of "a" and "b" - The determination of a and b for the case of the Cu_2S formed by the solid state reaction is straightforward. Equation (4) can be rewritten as

$$\frac{c}{A\epsilon_0} = \left(1 - \frac{b}{r_0}\right)^2 \frac{1}{a}$$

which shows that the plot $\left(\frac{c}{A\epsilon_0}\right)^{\frac{1}{2}}$ vs $\frac{1}{r_0}$ is a straight line with slope equal to $\frac{b}{\sqrt{a}}$ and intercept $\frac{1}{\sqrt{a}}$.

However when the Cu_2S is formed by the solution reaction the situation is more complex. From Equation (3) it can be seen that a plot of $\frac{c}{A\epsilon_0}$ vs l is a straight line the slope of which depends on b only. Therefore from the slope and the intercept of such a plot a and b can be determined. For a given material,

characterized by N_0 and r_0 , l can be varied by changing the solution reaction time t_s . Thus to be able to analyze the capacitance data, the grain boundary reaction rate has to be determined.

c) Grain Boundary Reaction Rate - The geometry of the grain boundary penetration is shown schematically in Figure 9, where the maximum depth of Cu_2S penetration, l , the skin thickness, d_0 , and the maximum grain boundary Cu_2S width, $2g$, are as indicated. Evidence for this type of geometry has been obtained by Scanning Electron Microscopy.⁽¹⁾ It is clear that l and g are both a function of the nature of the grain boundary as well as the reaction time. On the other hand θ may depend on the nature of the grain boundary but can be assumed to be independent of the reaction time.

Suppose an average Cu_2S thickness ($\bar{d}$) is determined by electrochemical methods.⁽¹¹⁾ By simple geometric arguments, It can be shown that

$$\bar{d} = L_A \times l \times g + d_0 \quad (5)$$

where L_A is length of grain boundary/unit surface area and l , g and d_0 were defined above.

Since L_A and g can be measured by quantitative microscopy a plot of $\bar{d}$ vs L_A will give l and d_0 independently. This method gives an average value of l over a large sample area. By repeating this experiment for different reaction times, the grain boundary reaction rate can be obtained.

Figure 9. Geometry of Grain Boundary Penetration.

To test the validity of the analysis presented above a thin layer of Cu_2S was formed on a set of as-deposited CdS samples by 6 second solution reaction. The grain boundary length of these CdS films had been previously determined. Table 1 gives the electrochemical thickness $\bar{d}$ and L_A where $\bar{d}$ is the average of three measurements.

Table 1

Average Cu_2S Thickness $\bar{d}$ and the Grain Boundary length/Unit Surface Area for Various CdS Films

Reaction Time: 6 sec.

Specimen #	$\bar{d}$ (Å)	L_A (mm ⁻¹)
238	2075	759
239	2024	519
242	2409	1085
265	1659	585.5
266	2321	901.0
267	2182	906
282	1981	687

The variation of $\bar{d}$ with L_A is shown in Figure 10. From this Figure we have:

$$d_0 = 1540 \text{ Å}$$

$$1 \times g = 7.7 \times 10^{-8} \text{ mm}^2$$

To measure g another CdS sample (#2-0982-12) was first mechanically polished down to .05 μm Alumina and then Cu_2S was grown on it by 6 seconds reaction after removing the Cu_2S by leaching in KCN, g was measured in an SEM. The average value thus obtained was 916 Å, which gives

$$l = 0.84 \text{ } \mu\text{m}$$

Figure 10. Variation of the average Cu_2S thickness, $\bar{d}$, with the grain boundary length/unit surface area, L_A .

As it was pointed out previously l and g individually depend (for a given reaction time) on whether the grain boundary is of low energy or high energy type. Metallographic studies performed on CdS grown in our laboratories indicate that some of the boundaries are of low energy type. However it is reasonable to assume that a relative number of low and high energy boundaries, over large areas does not change from sample to sample. Therefore the l and g values determined above are to the first approximation "universal" for a six second reaction time. These values give the semi-apex angle θ of the penetration (see Figure 9):

$$\theta = \tan^{-1} \frac{g}{l} = 6.2^\circ$$

Now, if all our assumptions are correct θ and l calculated here should be equal to the one directly measured from the SEM micrographs of Reference 4 (Figure 9, page 23) which shows the Cu_2S penetration for six second solution reaction. The values averaged over four boundaries of the micrographs are:

$$\begin{aligned} \theta &= 7.2^\circ \\ l &= 9545 \text{ \AA} \end{aligned}$$

These preliminary experiments show that our assumptions and methodology seem to be reasonably correct.

Major improvements in sample preparation are necessary to reduce the scatter in $\bar{d}$ vs L_A plots. The surfaces of CdS films should be mirror flat and damage free. This can be achieved by a final chemical or combined mechanical-chemical polish⁽¹²⁾ of the rough polished surfaces. A degree of etch attack is necessary to remove the damaged layer caused by mechanical polishing.

d) Shape of $C = N_D$ Contours - The analyses in the previous sections are based on the assumption that the $C = N_D$ contours are cylindrical in

shape. As a test of this assumption $C = N_D$ contours were plotted by a computer using the first 7 terms of equation (1). Figures 11 and 12 show these plots for $N_D = 10^{17} \text{ cm}^{-3}$ and $5 \times 10^{16} \text{ cm}^{-3}$ for different times and temperatures. The following numerical values were used for the generation of the plots:

$$\begin{aligned} r_0 &= 1 \text{ } \mu\text{m} \\ D_{11} &= 2.1 \times 10^{-3} \exp\left(-\frac{0.96 \text{ eV}}{kT}\right) \text{ cm}^2/\text{sec} \quad (13) \\ D_{\perp} &= 30 D_{11} \\ C_0 &= 6.6 \times 10^{22} \exp\left(-\frac{0.505}{kT}\right) \text{ cm}^{-3} \quad (13) \end{aligned}$$

It can be seen that at low temperatures, heat treatment times of up to an hour do not cause unacceptable deviation from the cylindrical geometry. However at high temperatures (185°C) the annealing times should not exceed a few minutes.

5.5 Phase E2.5 Illumination and Voltage Stress Tests

During this quarter the continuous illumination test facility has been completed and preliminary life tests started.

The experimental arrangement consists of a light source, hermetic enclosure to keep cells in pure argon and electronics to monitor temperature, open circuit voltage and to record I-V characteristics. A photograph of the test facility is shown in Figure 13.

The light source is made up of four 300 W ELH bulbs. There is another set of 4 bulbs as backup. When a bulb is blown during the test, one of the backup bulbs is automatically turned on. Such an arrangement permits indefinitely long illumination times without interruption. During the switchover

Figure 11. Boundaries of the compensated region in a cylindrical CdS grain. Grain diameter 2μ . Donor density 10^{17}cm^{-3} .

Figure 12. Boundaries of the compensated region in a cylindrical CdS grain. Grain diameter $2 \mu\text{m}$. Donor density $5 \times 10^{16} \text{ cm}^{-3}$.

Figure 13. Continuous illumination test facility.

to the backup bulb there is a slight change in the intensity which lasts 'till the new bulb reaches its normal operating condition. The influence of these temporal fluctuations in the light intensity on life test results is believed to be negligible.

The hermetic enclosure is identical to the one used in the roof top tests (Figure 24, Reference 1). The enclosure is continuously purged by high purity argon which goes through a Hydrox purifier (Matheson) before being introduced into the package. The purifier reduces the level of H_2O and O_2 in the argon down to 0.1 ppm level. At the present time the package can accommodate only one cell at a time. The cell is in contact with a thermoelectric temperature control block (Cambian) which keeps the cell temperature constant for the duration of the test.

During the test cells are kept at open circuit voltage and the value continuously monitored. Full I-V characteristics can be recorded as required.

Three cells have been tested under AM1 illumination. They were kept at open circuit voltage and at $28^{\circ}C$. The variation of V_{OC} as a function of time of illumination is shown in Figure 14. The behavior of the open circuit voltage is different in each case. Cell #21044.123 shows a linear decrease at a rate of 2.27 mV/hr. In the case of cell #21038.44 for the first 10 hours the V_{OC} decreases then stays constant for up to 125 hours. On the other hand the open circuit voltage stays constant for up to 500 hours in the case of cell #20675.B23. The relevant cell parameters at different stages during the test is given in Table 2. During the testing of cell #21044.123 the

Figure 14. Cell behavior under continuous illumination at open circuit voltage.

Table 2

Change in the Cell Parameters During Continuous Illumination Tests

<u>Cell #</u>	<u>V_{oc} mV</u>	<u>J_{sc} mA/cm²</u>	<u>FF %</u>	<u>η %</u>	<u>Comments</u>
21044.123	.5034	18.42	66.4	7.04	Initial Test
	.4415	16.16	47.0	3.84	After 42 Hours Testing. Light Hysteresis in I-V
	.4809	17.38	58.5	5.59	After Heat Treatment at 150°C in H ₂ for 16 Hours
20675.B23	.503	16.08	59.6	5.81	Initial Test
	.505	16.16	56.5	5.55	24 hours
	.505	16.32	56.1	5.57	48 hours
	.505	16.08	56.0	5.47	72 hours
	.505	16.24	55.5	5.49	144 hours
	.506	16.24	54.3	5.38	172 hours
	.504	16.08	56.1	5.48	480 hours
	.504	16.08	56.1	5.48	504 hours

facility did not yet have the capability to record I-V characteristics. As a result after 42 hours of testing, the cell was removed from the package and the I-V characteristic recorded in the Institute's main tester. Comparing the value of V_{OC} in Figure 14 and Table 2 it can be seen that there is a 10% increase. This difference is not due to the experimental artifact but rather to the fact that when the illumination is removed there is small but measurable recovery in V_{OC} .

This preliminary data shows that the behavior of the cells under these test conditions is complex and will require a large data base to permit separating the various mechanisms.

Phase E2.6 Multiple Stress Tests

This phase is scheduled to start in January.

6. FUTURE DEVELOPMENTS

The study of Cu_2S morphology on CdS and $(\text{CdZn})\text{S}$ cells will be continued with particular attention to the influence of deposition conditions.

Further testing of cells under open circuit voltage conditions will be carried out. Discussions with SES, Inc., may lead to some testing of IEC cells under their simulated sunlight conditions.

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