MASTER

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Critical Studies in Materials and Durability

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1. ABSTRACT

Characterization of the CdS and (CdZn)S substrate material has continued. The morphological differences between heterojunctions made by solid and solution reaction processes have been further detailed. The results of cell stability testing under open circuit and 0.3V loading are reported.

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3. INTRODUCTION

The research carried out on this contract is intended to provide fundamental materials understanding to support the cell development effort on XS-9-8309-1 and to study the basic mechanisms of cell degradation.

Scanning and transmission electron microscope examination of samples representative of CdS/Cu₂S and (CdZn)S/Cu₂S cells has continued. The behavior of various types of (CdZn)S/Cu₂S cells is shown to be reflected in the junction morphology.

An attempt to utilize photoluminescence and Auger/SIMS analysis to clarify the interaction of copper with defects in CdS was only partially successful.

Limited testing of a number of CdS/Cu₂S cells continues to indicate that at least some of the CdS/Cu₂S cells made recently are capable of sustained use under realistic loading conditions.

4. Task E1 Structure and Material Analysis

The grain size in CdS revealed by the SEM etching technique has been further checked using thin foils examined by TEM. In addition it has been concluded that the heat treatments used to optimise cells at $\sim 170^{\circ}\text{C}$ do not influence the grain or defect structure of the CdS. A range of cell formation procedures have been explored in the parallel cell development program XS-9-8309-1 and the corresponding junction morphologies have been studied using the Cu_2S stripping process. The characteristics of photoluminescence spectra at 77°K have been explored out to 1150nm and a photoluminescence technique for analyzing the Zn Content of $(\text{CdZn})\text{S}$ films has been developed.

4.1 Phase E1.1 Structure-Preparation Relation of CdS and $(\text{CdZn})\text{S}$ Layers.

Transmission Electron Microscopy (TEM) of CdS substrates grown at different rates (#1.0263, 1.0265 and 1.0266; average growth rates 2.0, 1.1 and $0.6\text{ }\mu\text{m/min}$ respectively) showed grains varying in diameter from 0.5 to $3.0\text{ }\mu\text{m}$. Substrate 1.0263 was the only sample showing a sufficiently normal distribution to allow a mean grain size of $1.5\text{ }\mu\text{m}$ to be deduced by TEM. The SEM etching technique gave $2.3\text{ }\mu\text{m}$ for this sample and 2.6 and $1.8\text{ }\mu\text{m}$ for 1.0265 and 1.0266 respectively. Figure 1 shows representative examples of small and large grains.

4.2 Phase E1.2 Influence of Heat Treatment and Ambient on CdS and $(\text{CdZn})\text{S}$.

The heat treatment at 170°C given to cells during optimization causes no detectable changes in the defect structure or grain size of the CdS.

Figure 2 shows typical grains following heat treatment which contain the usual density of line and planar defects.

The production of (CdZn)S films with the desired properties as deposited is proceeding well and it now appears unlikely that post deposition heat treatments will be necessary.

Figure 1: (a) and (b) Dark Field Image of Small Grains in CdS Layers.

Figure 1: (c) Example of Grains at the Large End of the Typical Size Distribution. Al Micrographs X 10,000.

Figure 2: Dark field images of grains in CdS substrate #1.0263 after heat treatment at 170°C.

- (a) Stacking Faults
- (b) Dislocations X 10,000

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

Experiments were performed to determine whether the photoluminescence characteristics of CdS could be used as a tool to examine copper diffusion into CdS. Incorporation of copper into CdS results in an enhancement in the red emission from the CdS. It should be noted, however, that red emission from the CdS may be due to a variety of impurity levels or defect states. Thus, the presence of the red emission does not specifically identify copper.

Four CdS samples were prepared for photoluminescence and Auger/SIMS analysis:

- (a) as-grown CdS
- (b) CdS solution reacted to form Cu_2S which was then removed with KCN and the CdS then heat treated
- (c) CdS solution reacted, heated to diffuse Cu, and then stripped with KCN
- (d) CdS coated with a 100Å copper layer by vapor deposition, heat treated and stripped with KCN.

The photoluminescence characteristics (450 to 1200nm) of the three samples, b, c and d were compared with the as grown CdS sample. The measurements were all made with the sample at 77°K using an excitation wavelength of 350nm. The photoluminescent spectrum of as grown CdS reported previously consists of:

- 1) An exciton peak at 490nm,
- 2) The green edge emission at 520nm,
- 3) A double peak at 720nm and 780nm,

The equipment available at IEC is limited to a wavelength of $\sim 800\text{nm}$. Utilizing the extended range to 1200nm in the Physics Department failed to reveal any further luminescence of significance.

The photoluminescent characteristics of sample (b) (barrier-stripped-heat treated) was nominally the same as the as grown CdS sample. However, the remaining two samples which were heat treated before the KCN strip, had an enhanced emission in the $720\text{-}780\text{nm}$ region as would be expected if copper diffused into the CdS. The increased emission in the $720\text{-}780\text{nm}$ region is measured relative to the exciton and edge emission.

All the above samples were sent to L. Kazmerski at SERI for Auger/SIMS analysis. The results of this examination were:

1. Sample (b) (barriered, stripped and subsequently heat treated) showed detectable amounts of copper along with zinc. The origin of the copper and zinc, is almost certainly from the back contact and is detected because of cracks or imperfections in the CdS layer.
2. No copper (or zinc) was seen in sample (c) (barriered, heat treated and subsequently stripped).
3. A large amount of copper was seen in the sample (d) (CdS coated with evaporated copper, heat treated and then stripped with KCN).

Thus no definitive conclusion could be drawn relating the $720\text{-}780\text{nm}$ peaks to copper incorporation in the CdS film. It has also been observed that when as grown samples of CdS are etched in HCl to remove the surface layer of CdS, an enhancement in the $720\text{-}780\text{nm}$ peaks is sometimes observed. Additional work to develop photoluminescence as a tool to investigate copper diffusion was deemed inappropriate since no correlation was seen with Auger/SIMS measurements and new, quantitative, photoluminescence apparatus would be required.

4.4 Phase E1.4 Quantify Defect and Grain Structure of Cu₂S

The morphology of the heterojunction for both CdS and (CdZn)S cells has been examined using the previously reported Cu₂S stripping procedure.⁽²⁾ A number of junction formation processes are being explored in the cell development program XS-9-8309-1 including solution and solid state Cu₂S reaction separately and in combination.

Cell 2.1026.121 was made by solid state followed by solution reaction on lightly textured CdS. The topography revealed in Figure 3 is similar to the previously reported solid state only cells (Reference 1, Figure 6b.) The example shown in Figure 3 reveals the fine texturing produced by the 20% HCl etching treatment and also shows large intrusions where the solution reaction has penetrated cracks in the solid state Cu₂S. Such intrusions are up to 20 μm in length, 2 μm deep and about 0.2 μm wide.

CdS cells grown on the smooth side of the electroformed copper lack the large (~ 10 μm diameter) pyramidal structure of the traditional CdS/Cu₂S cell. Wall intrusions are still observed, as shown in Figure 4a, but the spacing averages about 4 μm rather than 10 μm . The depth of the intrusions is the usual value of ~ 2 μm , but occasionally long thin intrusions penetrating ~ 10 μm were observed, Figure 4b. The origin of these defects is not clear.

The development program for (CdZn)S/Cu₂S cells is utilizing both solution and solid state reaction Cu₂S. Figures 5a and b show the morphology of a solid state reaction cell on lightly textured (CdZn)S (Cell #1.298.223). Shallow wall intrusions form with a spacing of about 15 μm and the pyramidal surface morphology produced by the etch is replicated. As seen in Figure 5b

the wall intrusions are discontinuous. Much more prominent and continuous wall intrusions are observed in the solution reaction cell #1.312.114 (Figure 6) in addition to deeper intrusions of up to 4 μm penetration.

A most surprising observation was made in this cell in that an intrusion free region was seen under a Au grid line (Figure 7.) No immediate explanation is obvious for this and further studies are planned.

$1\mu\text{m}$
↔

Figure 3: Junction Morphology of Cell #2.1026.121 Made by Solid State Reaction on Lightly Textured CdS Followed by Solution Reaction. X 10,000.

2 μ m
↔

Figure 4: (a) Intrusion Structure of Cell #2.1040.113 Grown on the Smooth Side of the Copper Sheet by Solution Reaction.

2 μ m
↔

Figure 4: (b) Needle Like Intrusion of $\sim 10 \mu$ m Length in the Same Cell. Both Micrographs X 10,000.

8 μ m
↔

Figure 5: Shallow Wall Intrusions in Solid State Reaction, Light Etched (CdZn)S. Cell #1.298.223. (a) X 1,250

4 μ m
↔

Figure 5: (b) X 2,500

2 μ m
↔

Figure 6: Cu_2S Intrusions in $(\text{CdZn})\text{S}/\text{Cu}_2\text{S}$ Cell #1.312.114 Formed by Solution Reaction on Lightly Etched $(\text{CdZn})\text{S}$. X 5,000

8 μ m
↔

Figure 7: Intrusion Free Region Under a Gold Grid Line.
(CdZn)S/Cu₂S Cell #1.312.114. X 1,250

5. Task E2 Cell Durability

Testing of cells under continuous illumination at V_{OC} and at 0.3V has continued. The study of the response of Cu_2S to oxidation and reduction has been impeded by difficulties in making suitable samples.

5.1 Phase E2.1 Controlled Oxidation--Reduction of Cu_2S

Complete conversion of thin (3000 Å) CdS films into Cu_2S was achieved by solid state reaction. Preparation of such thin films of Cu_2S on glass substrate has presented several problems. The coverage of CdS films tends to be non-uniform. This problem was solved by lowering the deposition temperature to 170°C. The second problem was the loss of adhesion of the Cu_2S films. This was observed within the reaction bath during the solution reaction and during the rinsing of cadmium chloride in the case of solid state reaction. Using careful surface cleaning procedures the loss of adhesion was significantly reduced for the solid state reaction. However, total loss of adhesion was still observed when the complete conversion is attempted with solution reaction.

Copper sulfide films obtained by the solid state reaction method were analyzed by EDAX. The results showed that within the detectability of the method and equipment used there were no impurities in the films (~ 1%).

5.2 Phase E2.2 Cell Response to Oxidation--Reduction

The sheet resistance of Cu_2S was measured as a function of oxidizing heat treatments using cells with interdigitated grid structure. However, the behavior of these cells during heat treatments showed that there were processing defects in them. Subsequent attempts to prepare cells with interdigitated grid structure have not yet been successful but a new set of cells are now in preparation.

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

Roof top exposure tests have been discontinued. The test method previously decided upon is under critical re-evaluation.

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

During this period experiments were continued to determine the grain boundary penetration rate of Cu_2S . A new polishing apparatus has been purchased which is used to prepare highly polished and damage-free CdS surfaces. The results of these experiments will be presented in the next reporting period.

55. Phase E2.5 Illumination and Voltage Stress Tests

Illumination/voltage stress test in the Institute test facility was continued. During these tests cells were kept at open circuit voltage and the V_{OC} decay recorded. Figure 8 shows the change in V_{OC} as a function of exposure for cell #21103.213 for a total of 30 days.

Figure 8: Change in V_{oc} during continuous illumination tests Load - at V_{oc} Temperature - 28°C illumination - AM]

The test facility is now connected to the Institute's computerized I-V measuring unit and the electrical characteristic of the cell under exposure can be periodically measured and results stored in a computer file. A new test enclosure is under construction which will permit the simultaneous exposure of up to eight cells.

5.6 Phase E2.6 Multiple Stress Tests

Several cells were exposed, in the Institute's facility and at SES, Inc., to continuous illumination under voltage and temperature stresses.

Cell 2.0675.B23 tested at the Institute at 50°C and open-circuit condition showed continuous degradation in V_{OC} . The same cell however tested at 28°C was stable for 400 hours.

Cells in two different packages are being tested in the test facility at SES, Inc. During these tests the temperature of the cells was 60°C and they were loaded to 0.3 Volts.

Figures 9, 10, 11 show the changes in V_{OC} , I_{SC} and FF respectively as a function of exposure days for three cells in package #1. In contrast cells in package #3 showed extremely rapid degradation. It is believed that this degradation is due to the reducing action of a potting compound on the Cu_2S .

SEQNO

PKNGID

122.

IEC1

CURVED BY: PKNGPOS

Fig. 9 Change in V_{OC} during continuous illumination tests at SES Inc.

Load: .3V

Temperature: 60°C

Illumination: AM1

SEQNO

122.

PKNGID

IEC1

CURVED BY: PKNGPOS

Fig.10 Change in I_{sc} during continuous illumination tests at SES Inc.

Load: .3V Temperature: 60°C Illumination: AM1

SEQNO

122.

PKNGID

IEC1

CURVED BY: PKNGPOS

Fig. 11 Change in FF during continious illumination tests at SES Inc.

Load: .3V Temperature: 60°C Illumination: AM1

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7. REFERENCES

1. IEC Progress Report XS-9-8310-1-02, April 1980
2. IEC Progress Report XS-9-8310-1-01, November 1979

APPENDIX

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