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Critical Studies in Materials and Durability

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1. Abstract

A summary of the structural and morphological features of CdS and (CdZn)S layers and their heterojunctions with Cu₂S is presented. The growth of the Cu₂S layer has been studied as a function of time for both the solution and solid state process using transmission electron microscopy. Preliminary observations have also been made on vapor and sputter deposited Cu₂S layers. The effect of oxidation and reduction heat treatments on the optical properties of Cu₂S are reported. Changes of cell performance with time for cells loaded to various points in the power quadrant are described.

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- B. J. Michael; K. H. Norian, D. B. Williams and J. W. Edington. STEM and CTEM Studies of the CdS Layer of Thin Film Solar Cells. European Electron Microscopy Meeting 1980 Proceedings pp. 352-353.
- C. K. H. Norian & J. W. Edington. A Microstructural Study of the Heterojunction Materials of the CdS-Cu₂S Solar Cell. 14th IEEE Photovoltaic Specialists Conference, pp. 700-705, 1980.

3. Introduction

The research carried out in this project is designed to support the cell development efforts under XS-9-8309-1 and to study the basic mechanisms of cell degradation.

Previous reports⁽¹⁻³⁾ have described the grain structure of the CdS and (CdZn)S films, the morphology of the CdS/Cu₂S junction and the results of preliminary durability measurements. The principal conclusions of these studies are summarized in this report along with the results of transmission microscope studies of the early stages of growth of the Cu₂S layer. Observations on Cu₂S layers prepared by vapor deposition and sputtering are also presented.

Results are reported on the optical properties of Cu₂S layers after reduction-oxidation treatments. Various cell stability test results are also reported.

4. Task E1. Structural and Materials Analysis

As a result of the work reported in references 1 through 3 a much more detailed knowledge has been gained of the structure of the CdS and (CdZn)S layers and the morphology of the heterojunction. Figure 1 is a schematic representation of the structure of the as-deposited CdS layers as deduced from scanning and scanning transmission electron microscopy. The heterojunction structure of wet and dry processed cells deduced from observations on Cu₂S stripped from completed cells is shown in Figure 2.

During this reporting period, the work on Cu₂S has been extended to examine the early stages of Cu₂S formation and also to look at Cu₂S layers produced by techniques other than the ion exchange process.

Nucleation and Early Stages of Growth of Cu₂S on CdS

The objective of this section of the work was to delineate the major features of the early stages of formation of Cu₂S on CdS formed by both the wet and the dry processes. The results are summarized below. The CdS was not etched before these experiments and the Cu₂S structure is, therefore, smoother than would be the case for textured solar cells. Two papers^(4,5) describing these results have been published and are reprinted as Appendices B & C.

1. The Wet Process

(a) Approximately 1 second dip time.

The Cu₂S coverage is 60%, but intrusions are already well developed, see Figure 3. In the regions where the Cu₂S film is not yet continuous, the growth process can be seen to be a sideways irregular growth, evident in Figure 4. Typically, intrusions have depths of penetration ranging between 0.2 and 3 μm . The advancing edge of the intrusions was irregular,

FIGURE 1. CdS microstructure based on conventional and scanning transmission electron microscopy.

FIGURE 2a. The structure of the CdS/Cu₂S heterojunction produced by solution reaction based on scanning and transmission electron microscopy studies of the Cu₂S layers stripped from CdS/Cu₂S solar cells.

FIGURE 2b. The structure of the CdS/Cu₂S heterojunction produced by solid state reaction, based on TEM and SEM studies of Cu₂S solar cells.

see Figure 4 and 6, and in a few cases appeared to be crystallographic, see Figure 6. Holes were also present in many of the intrusions, e.g. Figure 5. Careful examination of stereo pairs showed that the intrusions were hollow. Figures 7 and 8 show this graphically without the need for stereo pairs. All intrusions were cracked when viewed edge-on. From these observations it is deduced that the early stages of intrusion formation occurs in the manner shown schematically in Figure 9.

(b) Approximately 5 second dip time.

The Cu_2S film was still not continuous, see Figure 10. The whole form of the film and intrusion reconstruction was simply a more developed version of the 1 second specimen. Intrusions viewed edge-on still had two halves, see Figure 11, and were not continuous, Figure 12, and were very irregular. Within the errors of measurement the depth of intrusion growth did not appear to have increases significantly from the one second reaction time.

(c) 10 - 15 second dip time.

Films were almost continuous with only small areas of discontinuity. The intrusions were still apparently hollow and had not grown significantly. Figure 13 reproduced from Figure 2 reference 2, illustrates this.

2. The Dry Process

(a) Approximately 3 minute transformation.

The Cu_2S was not continuous, see Figure 14, and was cracked down the edges corresponding to the ridges on the growth pyramids of the CdS . Examination of the shallow intrusions showed that they were not continuous as shown in

FIGURE 3. Transmission electron micrograph of Cu_2S layer from Cell 2.1116. Cu_2S reaction time 1 sec and X 4000.

FIGURE 4. TEM of Cu_2S layer on Cell 2.1116, 1 sec and reaction time. X 11,300.

FIGURE 5. Cu_2S layer on Cell 2.1116, 1 sec and reaction time. Advancing front of Cu_2S intrusion. X 19,000.

FIGURE 6. TEM of Cu_2S layer on Cell 2.1116, Cu_2S reaction time 1 second. Advancing edge of Cu_2S intrusions. X 9,000.

FIGURE 7. Cu_2S layer on Cell 2.1116, Cu_2S reaction time 1 second. Direct evidence of hollow intrusions. 19,000.

FIGURE 8. TEM of Cu_2S layer on Cell 2.1116, reaction time 1 second. Further evidence of hollow intrusions. X 11,500.

FIGURE 9. Schematic illustration of growth of hollow Cu_2S intrusions.

FIGURE 10. TEM of Cu_2S layer on Cell 2.1116.22, reaction time 5 seconds. Cu_2S layer further developed but still showing discontinuities. X 4000.

FIGURE 11. Cu_2S layer on Cell 2.1116.22, Cu_2S reaction time 5 seconds. Intrusions still showing as hollow. X 11,500.

FIGURE 12. Cu_2S layer on Cell 2.1116.22, Cu_2S reaction time 5 seconds. Intrusions still showing as hollow. X 11,500.

FIGURE 13. TEM of Cu_2S stripped from CdS substrate 685M, reaction time 12 seconds. Intrusions still apparently hollow. X 4,000.

FIGURE 14. TEM of Cu_2S layer stripped from solid state cell, reaction time 3 minutes. Cu_2S noncontinuous and cracked along ridges of original CdS surface. X 4000.

FIGURE 15. Cu_2S stripped from solid state cell, reaction time 3 minutes. Noncontinuous intrusions. X 11,500.

FIGURE 16. Cu_2S stripped from solid state cell, reaction time 3 minutes. Cu_2S layer shows fringed shape to advancing front. X 11,500.

FIGURE 17. Transmission electromicrograph of evaporated Cu_2S layer from Cell 1.293.121. Generally continuous layer with point to point thickness variation. X 67,000.

17.

Figure 15. Stereo microscopy showed that the irregular shapes in the incompletely covered regions were "finger" shaped, see Figure 16, which shows this without the need for stereo viewing.

(b) Approximately 6 minute transformation.

There was more complete coverage, but the general features of the 3 minute transformation were all present. There had not, however, been appreciable growth of the "fingers" in the incompletely covered regions.

(c) Approximately 12 minute transformation.

The Cu_2S film was continuous as shown previously in Figure 6a of reference 2. Finger intrusions were still present however.

3. Influence of Microcleaners.

The general effect was to increase uniformity of coverage for conventionally treated wet and dry processed material.

Conclusions

1. Intrusions formed by the wet process are hollow.
2. Coverage of Cu_2S does not occur at a uniform rate for all faces of CdS for both wet and dry processed material.
3. Intrusions form very rapidly in wet processed material, but penetration slows with increasing dip time.
4. Coverage of slow growing regions of Cu_2S forms primarily by sideways growth from existing nuclei suggesting a ledge mechanism of film growth.
5. Coverage of Cu_2S is not uniform down the sides of intrusions during the early stages of growth.
6. Since deep grain boundary intrusions only form in the wet and not the dry process, the implication is that the cuprous chloride solution etches CdS grain boundaries.
7. Growth of finger intrusions in dry process may reflect some inhomogeneity in the CdS.

Cu₂S Layers Formed by Processes Other Than Ion-Exchange

With the cooperation of Dr. T. Vanderwel of McMaster University and Dr. J. A. Thornton of Telic Corporation samples of vapor deposited and sputtered Cu₂S were available for study.

Cu₂S morphology for evaporated Cu₂S.

Vapor deposited Cu₂S was on the HCl textured (CdZn)S base layer of cell #1.293.121. An estimated 800Å of Cu₂S was deposited at 5Å/second. Figure 17 is a transmission electron micrograph typical of the Cu₂S film from such cells. Although discontinuities are present, the total area of discontinuity is smaller than in cells grown by the solid state method⁽²⁾. However, discontinuities exist in the Cu₂S at points which correspond to the peaks of the (CdZn)S hills and may be due to a shadowing effect. A degree of terracing was observed in the Cu₂S corresponding to the sides of (CdZn)S hills. (Cells made by Vanderwel using IEC CdS⁽⁶⁾ achieved conversion efficiencies up to 6.2% with short circuit currents of 19 mA/cm².)

Heterojunction topography in mixed sulphide cells with sputtered Cu₂S

The Cu₂S thickness in Cell #1.293.1c was 3000Å, while that in #1.272.2c was 1000Å. Cu₂S was sputtered onto IEC CdS at a substrate temperature of 500°C and had a resistivity measured on a parallel glass substrate of 0.01 Ωcm. The (CdZn)S-Cu₂S heterojunction topographies for the two cells were examined using the SEM.

Figure 18 shows the heterojunction in cell #1.272.1c revealing the general morphology expected for un-etched (CdZn)S. The heterojunction contains small intrusions and some crack intrusions can be found (e.g. 'a' in Figure 18) which can be longer than 30 μm . Shorter crack intrusions run down the sides of hills. (e.g. 'b' in Figure 18.) Figure 19 shows more of the small intrusions and a crack intrusion, while Figure 20 shows that the small intrusions present throughout the heterojunction can on occasion penetrate deeply into the (CdZn)S. Figure 21 shows the presence of shallow wall intrusions and Figure 22 shows walls (w) at a high magnification.

The angular particles distributed across the whole surface may be an artifact of the sample preparation. They could also be the result of the sputtering conditions leading to the formation of copper nodules in addition to Cu_2S ⁽⁷⁾. The sample with 3000 $\text{\AA}$ of Cu_2S showed no such structure and, in fact, has a topography very similar to cells made at IEC using the solid state process.

Figure 23 shows the heterojunction on cell #1.293.1c with 3000 $\text{\AA}$ of Cu_2S . This resembles very closely IEC solid state cells. Figure 24 shows shallow walls, and a generally smooth texture on the rest of the heterojunction. Small spike intrusions, and as seen in Figure 25, thin crack intrusions are also present.

5. Task E2. Cell Durability

The optical properties of the Cu_2S layer are key to the performance of the $\text{Cu}_2\text{S}/\text{CdS}$ cell and its response to oxidation. In the first quarterly report⁽¹⁾ the theoretical modeling of a Cu_2S layer on glass was described. In this period progress in the experimental measurement of the response of Cu_2S to oxidation was made and is reported here.

1cm = 2 μ m

FIGURE 18. Sputtered Cu_2S layer from substrate 1.272.2c. Cu_2S thickness 1000Å. Particulates distributed generally across the surface. Shallow wall or crack intrusions are visible at a and b. X 5,000.

1cm = 2 μ m

FIGURE 19. Sputtered Cu_2S layer from substrate 1.272.2c. Cu_2S thickness 1000Å. Small crack intrusions visible at c. X 5000.

1cm = 0.5 μ m

FIGURE 20. Sputtered Cu_2S layer from substrate 1.272.2c. Cu_2S thickness 1000 $\text{\AA}$. Examples of particularly deep intrusions into the (CdZn)S layer. X 20,000.

1cm = 2 μ m

FIGURE 21. Sputtered Cu_2S layer from substrate 1.272.2c. Cu_2S thickness 1000 $\text{\AA}$. Further example of particulate and intrusions. X 5000.

1 cm = 1 μ m

FIGURE 22. Sputtered Cu₂S layer from substrate 1.272.2c. Cu₂S thickness 1000 $\text{\AA}$. High magnification view of shallow wall intrusions. X 10,000.

1cm = 4 μ m

FIGURE 23. Sputtered Cu₂S from Cell 1.293.1c, Cu₂S thickness 3000 $\text{\AA}$. Relatively featureless Cu₂S layer completely devoid of particulate structure observed on previous cell. X 2500.

23.

1cm = 2 μ m

FIGURE 24. Sputtered Cu_2S from Cell 1.293.1c, Cu_2S thickness 3000 $\text{\AA}$.
X 5000.

1cm = 2 μ m

FIGURE 25. Sputtered Cu_2S from Cell 1.293.1c, Cu_2S thickness 3000 $\text{\AA}$.
Crack intrusions. X 5000.

Further data has been acquired on the response of CdS/Cu₂S cells to exposure at the open circuit voltage and short circuit current points and also at 0.3V.

Controlled Oxidation--Reduction of Cu₂S

First order experiments on the optical characterization of Cu₂S films on 7059 glass has been started. The Cu₂S film used in this experiment had a thickness of 4400Å as measured by a profilometer. On the surface of the film some regions showed the presence of small ($\leq 1 \mu\text{m}$) nodules. These nodules were identified by energy dispersive x-ray analysis to be unreacted CuCl. The optical measurements were performed using regions of the film which did not have CuCl nodules.

The experiments consisted of measuring the total reflectance (R) and reflectance plus transmittance (R+T) in an integrating sphere (4π geometry) within the wavelength range of 0.4 to 1.6 μm . The results are shown in Figure 26 for three different heat treatments:

- Curve 1 after 37.5 hours in Ar 10% H₂ at 120°C
- Curve 2 after 17 hours in zero Grade Air (dry) at 80°C
- Curve 3 after 85 hours in zero Grade Air (dry) at 80°C

The most dramatic changes in these curves are in the long wavelength absorptance. This is mainly due to the free carrier absorption and increase with prolonged oxidation. Since it is expected that in fully stoichiometric chalcocite free carrier absorption is negligible, it is concluded that the initial reducing heat treatment was insufficient to reduce the film to complete stoichiometry.

FIGURE 26. Influence of oxidizing and reducing heat treatments on the reflection (R) and reflection plus transmission (R + T). See script for identification of each spectrum.

During the continuation of this contract the samples will be more strongly reduced to decrease free carrier absorption as much as possible before starting the oxidation heat treatments. Furthermore, the oxidation will be performed in both dry air and air with 50% relative humidity.

Interdiffusion and Cell Integrity Under Thermal Stressing

The first set of experiments to determine the grain boundary penetration rate of Cu_2S was inconclusive due to the wide scatter obtained from the electrochemical thicknesses of Cu_2S . It was found that during the chemical polishing of CdS films in aqua regia, a very thick layer was removed bringing the plane of observation into the region of small equiaxed grains. In this region, the assumption of cylindrical grains with vertical boundaries is not applicable. A new set of experiments are underway where the thickness of the removed layer will be more closely controlled.

Illumination and Voltage Stress Tests

During this period cell testing was continued in the present facility and a new test enclosure was built. The new enclosure will permit the testing of nine cell simultaneously.

Figure 27 summarizes the exposure test result of cell #2.1176.111. To determine the effect of load condition on the durability, during the first 11 days of the test the cell was kept at the short circuit point. During this period, as can be seen from Figure 27, the cell parameters were relatively stable. Following this the cell was tested at V_{OC} . Under this condition a marked drop in both V_{OC} and J_{SC} was observed. Further testing using sister cells tested simultaneously at V_{OC} and J_{SC} are planned using the new test facility.

FIGURE 27. Time dependent behavior of Cell 2.1176.111 under short circuit and open circuit loading conditions.

Multiple Stress Tests

Temperature and voltage stress tests were continued both in the Institute and at SES, Inc. More data were accumulated from the cells being tested at SES, Inc. under AM1 at 0.3V and 60°C. As reported in the previous quarterly progress report⁽³⁾, cells in package #1 are relatively stable whereas cells in package #3 suffered virtually total loss of short circuit current. Figures 28 and 29 show the variation of I_{SC} for cells in these two packages.

Cell #2.1103.213 were tested in the Institute's facility at 50°C. This cell has been under continuous illumination at 28°C for 30 days⁽³⁾ and showed a relatively stable V_{OC} . As shown in Figure 30, the V_{OC} was also stable at 50°C for up to a further 18 days of continuous illumination.

6. Acknowledgements

The continuing cooperation of Dr. S. DiZio, President, SES Inc. is gratefully acknowledged.

SEONO

PKNGID

122.

IEC1

29.

CURVED BY: PKNGPOS

CONTINUOUS ILLUMINATION TESTS AT SES INC.

LOAD : 0.3V ; TEMPERATURE : 60°C ; ILLUMINATION : AM1

FIGURE 28. Continuous illumination tests at S.E.S.Inc. Load 0.3 Volts, temperature 60°C, illumination AM1.

SEONO

134.

CURVED BY: PKNGPOS

PKNGID

IEC3

30.

CONTINUOUS ILLUMINATION TESTS AT SES INC.

LOAD : 0.3V ; TEMPERATURE : 60°C ; ILLUMINATION : AM1

FIGURE 29. Continuous illumination tests at S.E.S.Inc. Load 0.3 Volts, temperature 60°C, illumination AM1

IEC80313

FIGURE 30. Stability tests on Cell 2.1103.213 held at open circuit voltage.

7. References

1. IEC Progress Report XS-9-8310-1-01, November 1979.
2. IEC Progress Report XS-9-8310-1-02, April 1980.
3. IEC Progress Report XS-9-3810-1-03, October 1980.
4. J. Michael, K. H. Norian, D. B. Williams and J. W. Edington. Electron Microscopy 1980, Vol. 1 pp. 352-353.
5. K. H. Norian and J. W. Edington. 14th IEEE Photovoltaic Specialists Conference, pp. 700-705, 1980.
6. T. Vanderwel, R. Clarke, F. Schulz, D. Burk, N. Dalacu and J. Schewchun. 14th IEEE Photovoltaic Specialist Conference pp. 694-699, 1980.
7. W. W. Anderson and A. D. Jonath, Final Report AC02-77CH00178, June 1980.

Appendix A

Reports and Publications

Reports

1. IEC Quarterly Progress Report XS-9-8310-1-01, November 1979.
2. IEC Quarterly Progress Report XS-9-8310-1-02, April 1980.
3. IEC Quarterly Progress Report XS-9-8310-1-03, October 1980.

Publications

1. K. H. Norian & J. W. Edington, 14th IEEE Photovoltaic Specialist Conference, pp. 700-705, 1980.
2. J. Michael, K. H. Norian, D. B. Williams & J. W. Edington Electron Microscopy 1980, Volume 1 pp. 352-353.

Appendix B

J. Michael, K. H. Norian, D. B. Williams and J. W. Edington. STEM and CTEM Studies of the CdS Layer of Thin Film Solar Cells. European Electron Microscopy Meeting 1980 Proceedings pp. 352-353.

STEM AND CTEM STUDIES OF THE CDS LAYER OF THIN FILM SOLAR CELLS

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The CdS/Cu₂S heterojunction is the basis of a polycrystalline thin film solar cell that is one of the leaders in the race for commercial viability in terrestrial applications. Such solar cells have undergone extensive development, leading to considerable improvement in performance. Efficiencies in the range of 9% have been achieved. These are close to the U. S. Department of Energy goal of 10% for thin film cells.

The heterojunction consists of an epitaxial Cu₂S film, average thickness ~150nm, covering the top surface of a polycrystalline layer of CdS ~25-30μm thick. The CdS film is produced by rapid evaporation onto an electroformed copper foil. Although the perfection of the CdS layer is critical to the cell performance, the microstructure has not been studied in modern efficient cells. This paper summarizes the results of a recent CTEM and STEM study.

CdS layers 25-30μm thick were grown by vapor deposition at 2μm/min (substrate temp. 220°C) and thinned for electron microscopy by ion beam bombardment. Figure 1 shows an electron micrograph typical of the top half of the film. Bend contours arise from the elastic strain produced by differential thermal contraction between the CdS and the copper substrate during cooling after deposition. The grain size is ~2μm with occasional grains 10-15μm in diameter, while at the back surface it is 10-50nm (fig. 2). The average dislocation density was ~10⁹ cm⁻². Grain boundaries were irregular and triple points did not meet at equilibrium angles. The growth direction of most of the grains in the top half of the layer was within ~5° of the c axis. However ~20% showed a large deviation (10-25°). All the above features are consistent with classification (1) under zone 1 as defined for thick films grown at a fast rate.

Ultra-fine grained regions ~2-15μm in diameter were observed in the top layers of some CdS films (fig. 3). STEM-X-ray microanalysis showed that these were of two types. Some contained Cd and S only, while others were contaminated with Si and Cl, see inset X-ray spectrum taken from outlined region in fig. 3. In both regions the grain size was ~0.2μm and in neither was there a detectable preferred growth direction. These are "spits" of material ejected directly from the evaporation source. Chlorine is an impurity in the source CdS, whereas Si probably arises from the glass wool used as a baffle in the evaporation source.

The essential features of the CdS film are summarized in fig. 4. Dislocations and grain boundaries are relevant to cell performance because they are reproduced in the epitaxial Cu₂S layer. They will act as recombination sites and reduce the current generated by the cell. Spits contaminated with Cl and Si will develop local modifications in the energy band diagram of the heterojunction. This would be expected to reduce the short circuit current, I_{sc} , and the open circuit voltage V_{oc} .

This project was supported in part by the Solar Energy Research Institute under subcontract XR-9-8063-1.

1. J. A. Thornton, Ann. Rev. Mat. Sci., 7, 239-260, 1977.

Fig. 1 Bright field image of typical region near the top of CdS layer.

Fig. 2 Centered dark field image of CdS grains at CdS/Cu interface.

Fig. 3 Bright field image of fine grained region of CdS. X-ray spectrum from region outlined.

Fig. 4 Schematic diagram illustrating the essential features of CdS layer.

Appendix C

K. H. Norian & J. W. Edington. A Microstructural Study of the Heterojunction Materials of the CdS-Cu₂S Solar Cell. IEEE Photovoltaic Specialists Conference, pp. 700-705, 1980.

A MICROSTRUCTURAL STUDY OF THE HETEROJUNCTION MATERIALS OF THE CdS-Cu₂S SOLAR CELL

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ABSTRACT

The grain size, dislocation density, and microscopic defect structure of CdS films used in photovoltaic cells have been determined. In addition the topography of the CdS-Cu₂S interface has been studied. The major features of the Cu₂S films and the common features of the interface have been delineated. Moreover the various types of defects that can occur if the material is not grown under ideal conditions are described. Most of these can be avoided by proper control of film growth conditions. The influence of defects on the electrical properties of the cell is discussed.

INTRODUCTION

Solar cells, based on the CdS-Cu₂S heterojunction have been the subject of extensive research. As a result, techniques for producing devices have been refined to enable formation of films with a comparatively low density of defects. The purpose of this paper is to summarize the results of recent studies of morphology of CdS and Cu₂S films. In addition a description has been included of the types of defect that can occur if growth conditions are not properly controlled.

EXPERIMENTAL

Cadmium sulfide films 25-30 μm thick were produced by vapor deposition at rates of approximately 1 $\mu\text{m}/\text{min}$ unless stated otherwise. Copper sulfide layers were grown on the top surface by either the solution method (1) or the solid state reaction (2). The solution process consists of immersion of the etched CdS in an aqueous solution of Cu₂Cl₂ held at 100°C. In the dry process the Cu₂Cl₂ is evaporated onto the CdS and the two films are reacted by heating at 170°C. Prior to the Cu₂S growth from solution, the CdS was etched for 2 seconds in 55% HCl. However for the solid state process reported here there was no etching step.

Examination of the CdS and Cu₂S was conducted using SEM and TEM. TEM specimens of CdS were produced by argon ion beam thinning (3 kV, 25 μA). The copper substrate was removed with concentrated ammonium persulfate solution before final thinning. Copper sulfide specimens were produced by lifting off the layer from the CdS by dissolving the latter in 33% HCl over a period of between 2 and 4 hours (3).

RESULTS AND DISCUSSION

CdS Microstructure

The major features of CdS films are shown in Figure 1. The topography of the top CdS surface follows that of the electroformed copper substrate and contains hills and valleys. The hills were partially faceted and were approximately 5 μm high with a baseline between 10 and 15 μm . At the top and center of the film the average grain diameter is approximately 2 μm but is reduced to less than 1 μm near, and 10-50 nm at, the copper substrate surface.

The growth direction of the majority of the CdS grains is within $\pm 5^\circ$ of the c axis but many show a large deviation ($10-25^\circ$). Misorientations across the grain boundaries are typically in the range $5-25^\circ$. Most grains contain a dislocation density of approximately 10^9 cm^{-2} (Figure 2). In addition planar defects frequently occur that may be stacking faults or antiphase domain boundaries. Some regions (2-15 μm in diameter) contain Si and Cl (2 to 10%) and have a fine grain size (approximately 0.2 μm). These regions probably correspond to "spits" that arise if particles of the evaporant are emitted directly from the source to become embedded in the surface of the CdS film as it grows. Typically such defects are approximately 2-15 μm in diameter, and are loosely attached to the main CdS film. Spits become common if the rate of deposition of the CdS is increased above $\sim 2.5 \mu\text{m}/\text{min}$. The density of contaminated spits varies between 0 and 5% of the top surface of the film, depending on the substrate. The morphology of the CdS film is consistent with classification under Zone 1 as defined for thick films grown at a fast rate (4).

Etching prior to Cu₂S formation produces crevices at the bottom of the valleys and at grain boundaries. Holes up to approximately 20 μm in diameter may also develop as a result of etching. Etching produces pyramids with hexagonal bases of the order of microns or less (Figure 3).

Morphology of Cu₂S and topography of CdS-Cu₂S heterojunction

Cells grown by the solution method. The thickness of the Cu₂S films grown by the solution method was not uniform because the Cu₂S forms as caps on the pyramids developed during the etching step. Figure 4 illustrates the topography of the

film schematically. For a Cu_2S film with an equivalent thickness of 160 nm, the centers of the caps are thicker than the edges; the latter being a few tens of nm thick. Depending on the film, the CdS- Cu_2S interface may be terraced or smooth as illustrated in Figures 4, 5 and 6. Moreover, discontinuities exist between clusters of Cu_2S caps.

In addition to the above general features of the Cu_2S film, 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 (Figure 7). 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 tops of the walls are frequently cracked with displacements of 10 to 150 nm. The origin of these cracks is not clear at present but may be a result of the mismatch strain acting along the plane of the Cu_2S film.

The following types of intrusion are occasionally present in different films. They are all illustrated schematically in Figure 8.

1) Ring intrusions - These intrusions 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. 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.

3) Spit intrusions - These defects are so named because they are believed to arise from "spits" in the CdS described earlier. They consist of large, uneven hollow penetrations of Cu_2S up to approximately $20 \mu\text{m}$ in width at the base and up to $17 \mu\text{m}$ deep. Partially formed spit intrusions are also observed that consist of several pointed curved intrusions that penetrate up to a depth of approximately $3.5 \mu\text{m}$, and are illustrated in Figure 8.

Spit intrusions occur when the interface between loosely bonded spits 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. 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 approximately $4 \mu\text{m}$; at least twice that of the wall itself. The tips may be sharp or blunt.

Cells grown by the solid state reaction

The details of these films are much simpler than those produced by the solution process. Examination of stripped Cu_2S films shows that shallow wall intrusions penetrate less than $1 \mu\text{m}$ into the CdS valley bottoms and the occasional shallow cone intrusions penetrate less than $0.5 \mu\text{m}$ into the sides of the CdS hills near valley bottoms. The CdS- Cu_2S interface has a terraced structure and the only major defects that develop in the film are cracks and holes (Figures 9, 10 and 11). The holes appear because of unreacted Cu_2Cl_2 which is dissolved by the HCl during specimen preparation.

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. These are discussed below.

1. Spits in the CdS layer that contain high levels of Si and Cl contamination will lead to local modifications in the energy band diagram of the heterojunction. This will increase losses in short circuit current, I_{sc} and open circuit voltage, V_{oc} .

2. Variations in the junction area from cell to cell arising from differences in the number and size of intrusions will lead to differences in V_{oc} . In heterojunctions of maximum disorder where all types of intrusions are present, low values of V_{oc} would be expected. Experimentally it has been found that the appearance of ring intrusions can lead to a reduction in V_{oc} of up to 30 millivolts. This compares well with the calculated value of 20 mV obtained by substituting junction area measurements from electron micrographs in the relation (5).

$$V_{oc} = \phi + \frac{kT}{q} \ln \frac{J_{sc}}{qN_{c2}s_1} - \frac{kT}{q} \ln \frac{A_j}{A_1}$$

Where

J_{sc} = short circuit current density

q = electronic charge

s_1 = interface recombination velocity

ϕ = activation energy as described elsewhere (5)

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

A_j = junction area

A_1 = planar area

3. Intrusions with pointed tips 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 and a decrease in V_{oc} (6). Another effect of the increase in temperature is that Cu vacancies are generated in the Cu_2S and Cu is driven out of the Cu_2S (7). In confirmation of this theory, nodules up to approximately 1 μm in diameter have been observed at the tips of some intrusions of cells that have been exposed to sunlight (Figure 12). This is illustrated schematically in Figure 8. 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 and this causes a further decay in V_{oc} with time. Extensive growth of copper on the tip of deep cone intrusions may eventually lead to shorting of the Cu_2S to the back contact of the cell.

4. The observed variation in the thickness of the Cu_2S will 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 I_{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 I_{sc} .

5. 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 (8).

6. The discontinuities in the Cu_2S film—cracks, holes, or gaps between Cu_2S caps—will reduce V_{oc} , I_{sc} and fill factor. Such defects may also cause shorts between the collection grid and the CdS if they are large enough.

CONCLUSIONS

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

1. The grain size, dislocation density, and planar defect distribution in CdS grown under typical conditions has been characterized.

2. Spits contaminated with Si and Cl have been identified in CdS films.

3. Copper sulfide films grown by the solu-

tion method have all been shown to contain wall intrusions that correspond to the bottom of valleys in the CdS. Such films are noncontinuous, and the interface with the CdS may be smooth or terraced.

4. 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.

5. A number of defects in solid state reacted Cu_2S films have been identified, including holes, cracks and terraced interfaces arising from the growth process.

6. Defects including high intrusion density, sharply pointed intrusions, variations in Cu_2S thickness and continuity as well as spits in the CdS, usually degrade the performance of a cell.

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Figure 1 Schematic representation of CdS film

Figure 3 SEM micrograph showing pyramids on surface of CdS film

Figure 2 TEM micrograph showing dislocations in CdS grains

Cu₂S - CdS MORPHOLOGY, BASED UPON TEM AND SEM STUDIES OF Cu₂S REPLICAS

Figure 4 Cross-section of Cu₂S - CdS heterojunction for solar cell grown by solution method

Figure 5 TEM micrograph of Cu_2S film showing Cu_2S caps with a smooth interface

Figure 7 SEM micrograph of Cu_2S film showing wall intrusions

Figure 6 TEM micrograph of Cu_2S film showing caps with a terraced interface

Figure 8 Three-dimensional representation of topography of Cu_2S - CdS heterojunction showing different types of Cu_2S intrusions

Cu_2S - CdS MORPHOLOGY, BASED UPON TEM AND SEM STUDIES OF Cu_2S REPLICAS

Figure 9 Cross-section of Cu_2S - CdS heterojunction for unetched dry cell

Figure 11 SEM micrograph of Cu_2S film from unetched dry cell showing terraces and cracks

Figure 10 TEM micrograph of Cu_2S film from unetched dry cell showing terraces