300
11/24/80
1-5

Dr. 2100

(2)

MASTER

SERI/PR-9075-1-T1

**MATERIALS STUDIES RELATED TO THE $\text{Cu}_2\text{S}/\text{ZnCdS}$
HETEROJUNCTION**

First Quarterly Report for Period March 15—June 15, 1980

By
L. C. Burton

July 1980

Work Performed Under Contract No. AC02-77CH00178

Virginia Polytechnic Institute & State University
Department of Electrical Engineering
Blacksburg, Virginia

DIST-231
NTIS-25

U.S. Department of Energy

2104

Solar Energy

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.

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 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."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$6.00
Microfiche \$3.50

MATERIALS STUDIES RELATED TO
THE $\text{Cu}_2\text{S}/\text{ZnCdS}$ HETEROJUNCTION

FIRST QUARTER REPORT No. SERI/9075/QPR-1

SERI SUBCONTRACT No. XS-0-9075-1

TIME PERIOD: 3/15/80-6/15/80

L. C. BURTON - PRINCIPAL INVESTIGATOR

July 1980

Department of Electrical Engineering
Virginia Polytechnic Institute & State University
Blacksburg, VA 24061

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

ABSTRACT

Work over the first quarter was directed toward compositional measurements of $\text{Cu}_2\text{S}/\text{ZnCdS}$ junctions by AAS and AES, and modelling of the junction based on these measurements. AAS and AES measurements both indicate an accumulation of Zn under the interface. AES profiles indicate Zn and Cd in the Cu_2S , although AAS indicates concentrations below $5 \times 10^{19} \text{ cm}^{-3}$. A model based on lateral composition variation at the interface is presented. This model can account for some of the trends seen in $\text{Cu}_2\text{S}/\text{ZnCdS}$ cells, especially the decrease in short circuit current at higher Zn compositions.

TABLE OF CONTENTS

	<u>page</u>
ABSTRACT	
1. INTRODUCTION	1
2. TECHNICAL NARRATIVE	1
2.1 COMPOSITIONAL MEASUREMENTS	1
2.2 MODELLING	9
3. FUTURE WORK	9
REFERENCES	10
4. PARTICIPANTS	11
5. APPENDIX	13

1. INTRODUCTION

This is the First Quarterly Report for SERI Sub-contract XS-0-9075-1, "Materials Studies Related to $\text{Cu}_2\text{S}/\text{ZnCdS}$ Heterojunctions". The time period of the contract is 3/15/80 - 3/14/81 and the amount is \$65,289.

Work over the past few years related to $\text{Cu}_2\text{S}/\text{ZnCdS}$ cells was recently reviewed.⁽¹⁾ In summary, cells of this type have produced higher V_{oc} but lower J_{sc} than for $\text{Cu}_2\text{S}/\text{CdS}$ cells. The decrease in current has been attributed to Cu_2S degradation, to an interfacial spike and to modified properties of base (ZnCdS). The major objective of this program is a better understanding of device operation, by means of compositional and electro-optical measurements plus modelling, which can potentially lead to improved fabrication techniques and increased photoresponse.

Program tasks are presented below, in summarized form.

Task 1. Compositional (AAS and AES/ESCA) measurements of $\text{Cu}_2\text{S}/\text{ZnCdS}$ and $\text{Cu}_2\text{S}/\text{CdS}$ junctions fabricated by wet and dry techniques. (Includes Cu_2S composition, concentrations of Zn, Cd and Cu near the interface, and depth profiling)

Task 2. Electro optical studies of devices. (Includes I-V and Cu_2S sheet resistance measurements)

Task 3. Junction capacitance studies, including photocapacitance.

Over this quarter, work was mainly related to Task 1, dealing with compositional measurements and analysis thereof.

2. TECHNICAL NARRATIVE

2.1 Compositional Measurements

Measurements were made on various regions of $\text{Cu}_2\text{S}/\text{ZnCdS}$ junctions

using AAS and AES* techniques. Mostly wet-formed junctions were measured, made on ZnCdS substrates supplied by the University of Delaware. Some dry processed junctions have also been formed and analyzed by AAS.

Atomic Absorption Measurements

Initial AAS results related to compositional studies of various regions of the junction have been published.⁽²⁾ The following solutions have been measured for ZnCdS powder, films and single crystals over a wide range of compositions: 1) an initial HCl etch to determine base composition (tests were done to preclude preferential etching artifacts); 2) the Cu^+ ion exchange solution (wet process), or the post-formation rinse (dry process); 3) KCN solution in which the Cu_2S layer was removed; 4) several subsequent HCl etches of the base material following Cu_2S stripping; 5) HCl, KCN and barrier solution blanks.

Several trends have been apparent for all samples measured. These are indicated in Table 1 and Figure 1 for wet processed Cu_2S .

Table 1. Zn/Cd mass ratios for three sample types, for three types of ZnCdS.

<div style="text-align: center;">ZnCdS type Sample</div>	Thin Film	Powder	Single Crystal
Base Material	0.162	0.121	0.063
Cu^+ Solution	0.093	0.096	0.048
Post HCl Etch	1.52	0.296	0.360

* Measurements performed at University of Illinois, Coordinated Science Laboratory (Prof. J. E. Greene)

Fig. 1. Composition (x in $\text{Zn}_x\text{Cd}_{1-x}\text{S}$) of ZnCdS layer below interface as function of etch time (a) and Cu_2S formation time (b).

The post HCl etch was performed directly after Cu_2S removal. For several samples, a number of etches were made in succession (Fig 1a). Results related to the KCN solutions are not shown in the table because the amounts of Zn and Cd found were near the resolution of the spectrophotometers, making Zn/Cd ratios fluctuate widely. (This is related to Zn and Cd content of Cu_2S , and will be discussed in more detail shortly.)

From these measurements, the following points are of interest:

1. The Cu^+ solution is Zn deficient..
2. The base region under the interface has an excess of Zn.
3. There is less than 0.1% of Cd and Zn retained in the Cu_2S .

The enrichment of Zn beneath the interface, for wet processed junctions) depends on Cu_2S formation time, as expected. Results are shown in Fig 1b indicating this, for junctions made from one thin film substrate, of nominal 8% Zn content (coaxially deposited; obtained from University of Delaware). A substantial enhancement of Zn content is still obtained for formation times of 10-15 sec.

From the AAS measurements beneath the junction, only a gross picture can be obtained. This region is probably very non-homogeneous in all directions, especially very near the interface (within $\approx 0.1\mu\text{m}$). The 10% HCl etch removes about $500\text{\AA}$ per minute of ZnCdS material, over the entire surface. Therefore, a 30 sec etch (roughly the minimum allowed to obtain enough material for reliable AAS data in a 20 ml volume) removes several hundred angstroms of this highly non-homogeneous region, perhaps preferentially. Therefore, from these measurements we cannot say anything about the distribution of Zn (except that it decreases away from the junction) or about the atomic/crystallographic nature of the "ZnCdS" that exists here.

The fact that the ion-exchange reaction rate is crystallographically anisotropic⁽³⁾ leads to the conclusion that the Zn accumulation is laterally non-homogeneous. For dry processed junctions that are non-planar, the Cu_2S will have non-uniform thickness and a similar conclusion applies. Therefore, junctions pertaining to Fig 1. can be viewed as a distributed array of junctions of varying composition. Such a model is discussed in the Appendix.

For dry processed junctions, the results are similar, although more severe for the few samples thus far measured. The solid state reaction temperature is 130°C , and the Zn/Cd ratios found in the post-reaction rinses (where the CdCl_2 and ZnCl_2 are washed off the Cu_2S surface) are less than those found in the Cu^+ solution for wet processed Cu_2S . It thus appears that differences between the $\text{Cd}^{++} \rightarrow 2\text{Cu}^+$ and $\text{Zn}^{++} \rightarrow 2\text{Cu}^+$ ion-exchange rates become even greater at 130°C than at the 95°C temperature of the wet reaction.

We have consistently not been able to find significant amounts of Zn or Cd in Cu_2S formed on ZnCdS or (for Cd) on CdS using AAS. The resolution of the spectrometers for Zn and Cd is about 0.001 mg/l of solution. We measure typically 0.01 - 0.02 mg/l of Zn and 0.002 - 0.01 mg/l of Cd. For a Cu_2S layer 1 μm thick and 2 cm^2 in area, the above sample concentrations translate into the following atomic concentrations in the Cu_2S .

$$\text{Zn: } 2 - 4 \times 10^{19} \text{ cm}^{-3}$$

$$\text{Cd: } 4 \times 10^{18} - 2 \times 10^{19} \text{ cm}^{-3}$$

A concentration of $2 \times 10^{19} \text{ cm}^{-3}$ is about 0.05 at % ($4 \times 10^{22} \text{ cm}^{-3}$ of Cu in Cu_2S).

Other investigators have deduced the presence of up to one atomic percent of Cd in Cu_2S formed on CdS .⁽⁴⁾ In order to make sure that our Zn and Cd

measurements were not being hidden by interference effects, Zn^{++} and Cd^{++} standard solutions were diluted in the same matrix resulting from Cu_2S dissolution (Cu_2S dissolved in 0.1 M KCN). The resulting Zn and Cd values measured were the same as the mixed values to within experimental uncertainty. It thus does not appear that Zn and Cd in the Cu_2S are masked by other species in the solution. (There is a Cu line at 216.5 nm, which is not close enough to the 213.9 nm Zn line to interfere with it.) These considerations lead to the conclusion that the above metal concentrations in the Cu_2S are probably reliable. This does not preclude the possibility that there are segregated patches of say ZnS somehow inbedded in the Cu_2S , which do not dissolve the KCN solution. There is excess Zn detected below the interface. However, it is not clear how this Zn could originate from the Cu_2S as the Cu_2S is etched off.

It should also be noted that AES measurements (discussed next) indicate Zn and Cd segregation on the Cu_2S surface. This probably accounts for a fraction of the Zn and Cd attributed to the Cu_2S , although what fraction is not clear.

Auger Measurements

Several $\text{Cu}_2\text{S}/\text{ZnCdS}$ samples made on single crystal and IEC thin film material were measured via AES at the University of Illinois Coordinated Science Laboratory.* Because of the direct bearing on this project, some of these results are discussed below.

1. An Auger profile (using Ar^+ milling) of a ZnCdS film (starting

* Acknowledgement and thanks are extended to Prof. J. E. Greene and to Ms. L. Rivaud for performing these measurements.

composition, $x = 0.2$) following removal of the Cu_2S layer verified the enhancement of Zn deduced from AAS measurements on similar samples. In fact the decay of x from 0.7 to 0.3 going into the bulk agreed well with the decay of from 0.63 to 0.26 found using AAS (Fig 1a). A virgin ZnCdS sample was also profiled to preclude the possibility of sputtering artifacts - these composition curves were flat.

An Auger profile through a $\text{Cu}_2\text{S}/\text{ZnCdS}$ junction formed on $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ single crystal material is shown in Fig 2. There are several features of interest:

1. Enhanced Zn, Cd, Cl and O amounts exist on the Cu_2S surface. Similar results have been reported for CdS cells.⁽⁵⁾ The O signal results at least in part from oxidized Cu, and the Cl is probably a remnant of the ion-exchange. The origins of Zn and Cd are not apparent.
2. A substantial Zn signal remains in the bulk Cu_2S , as does a smaller one for Cd (discussed below).
3. A rapid increase is seen in Zn composition (prior to that of Cd). (Atomic Zn/Cd ratios at three locations are indicated in the figure).

The latter result is consistent with the profile of Fig 1, and with the analogous Auger profile on a similar sample discussed earlier. From Fig 2 it appears that this Zn enhanced region extends from below the interface into the Cu_2S . A similar situation has been proposed for Cd in Cu_2S .⁽⁶⁾ However, any interpretation related to the location of the Zn rich region must take into account mechanical effects of the ion-milling which is often a difficult task. As indicated in Fig 2, Zn/Cd atomic ratios as large as 12 exist in this Zn rich region.

Although the Zn and Cd signals approach zero in the Cu_2S , their

Fig. 2. Auger profile of $\text{Cu}_2\text{S}/\text{ZnCdS}$ junction formed on $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ single crystal, using Xe^+ ion-milling.

signals still exist, especially for Zn, as the milling proceeds. There are several possibilities:

1. There is $\sim 1\%$ of Zn and Cd in the Cu_2S ,
2. Some of the surface Zn and Cd is still being detected or being driven into the bulk,
3. Zn and Cd signals could result from cracks in the $\text{Cu}_2\text{S}^{(3)}$, allowing a small area of ZnCdS to be sampled and recorded.

Due to the difficulties inherent in accurately interpreting compositions from AES profiles of rough polycrystalline layers, it is felt that the AAS data for Zn and Cd concentrations in Cu_2S are at present more reliable. An upper limit for Zn in wet formed Cu_2S on $\text{Zn}_{0.2}\text{Cd}_{0.8}\text{S}$ is about $5 \times 10^{19} \text{ cm}^{-3}$, with Cd about a factor of two lower.

2.2 Heterojunction Modelling

Based in part on the previous measurements, a modified model has been devised for the $\text{Cu}_2\text{S}/\text{ZnCdS}$ heterojunction. This model was presented at the 22nd Annual Electronic Materials Conference at Cornell University (June 27, 1980). A copy of the paper is attached in the Appendix.

3. FUTURE WORK

The major emphasis over July - September will be the formation and study of gridded junctions (i.e. cells). Thin film $\text{Cu}_2\text{S}/\text{ZnCdS}$ and $\text{Cu}_2\text{S}/\text{CdS}$ cells will be made by the wet and dry processes on substrate supplied by the University of Delaware.* Compositional measurements will also continue on a smaller number of samples, especially dry processed ones. Additional AES data will also be forthcoming.

* Drs. John Meakin and Bob Hall of IEC are kindly acknowledged for their assistance in supplying substrate material.

REFERENCES

1. L. C. Burton, Solar Cells 1, 159 (1980)
2. L. C. Burton, Appl. Phys. Lett. 35, 780 (1979)
3. L. R. Shiozawa, et al, Report ARL 69-0155 (Clevite Final Report, 1969)
4. J. J. Loferski, et al, Solar Energy Materials 1, 157 (1979)
5. J. D. Meakin, CdS Solar Cell Workshop Proceedings, p.84 (University of Delaware, 1975)
6. H. W. Brandhorst, 7th Photovoltaic Specialists Conference Proceedings, p. 33 (1968)

4. PARTICIPANTS

L. C. Burton, Principal Investigator, Associate Professor of Electrical Engineering.

D. Dwight, Faculty Participant, Assistant Professor of Materials Engineering.

P. Uppal, Graduate Assistant (Physics).

W. B. Hsu, Graduate Assistant (EE).

T. Nyamusa, Graduate Assistant (EE).

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

5. APPENDIX

Paper presented at 22nd Annual Electronic Materials Conference,
Cornell University (June 27, 1980)

MEASUREMENT AND MODELING OF Laterally

Graded Photovoltaic Heterojunctions*

by

L. C. Burton, W. B. Hsu and P. Uppal[†]
Departments of Electrical Engineering and Physics[†]
Virginia Polytechnic Institute & State University
Blacksburg, VA 24061

*Supported by the Solar Energy Research Institute

ABSTRACT

A model is presented for the $\text{Cu}_2\text{S}/\text{Zn}_x\text{Cd}_{1-x}\text{S}$ heterojunction that is based on the existence of a laterally graded zinc rich region just below the Cu_2S - ZnCdS interface. The increase in open circuit voltage and decrease in short circuit current that result are in substantial agreement with experimental results for junctions formed by aqueous ion-exchange.

INTRODUCTION

$\text{Cu}_2\text{S}/\text{Zn}_{1-x}\text{Cd}_x\text{S}$ junctions have resulted in higher open circuit voltages (V_{OC}) than those of $\text{Cu}_2\text{S}/\text{CdS}$ solar cells.⁽¹⁻⁴⁾ However, the ZnCdS types consistently generate lower short circuit currents (J_{SC}) than similarly fabricated CdS cells. This problem has been especially more severe for higher zinc composition base material ($\sim 20\%$ zinc).^(4,5)

All reported $\text{Cu}_2\text{S}/\text{ZnCdS}$ junctions have been formed by means of ion-exchange. It has been shown that the ion-exchange process, when used with the ternary compound (ZnCdS), results in an accumulation of Zn near the Cu_2S -ZnCdS interface.⁽⁶⁾ It has been proposed that this effect can account for some of the unexpected differences between CdS and ZnCdS based cells, the most salient one being short circuit current reduction for ZnCdS cells. (The V_{OC} increase for ZnCdS based cells is anticipated; a decrease in J_{SC} for atomic Zn percentage up to about 40% is not.)

This decrease in photogenerated current can potentially be attributed to degraded properties of the Cu_2S or to decreased transmission at the interface, including increased interface recombination. Our previous composition measurements have indicated that an excess amount of Zn is retained near the Cu_2S -ZnCdS junction, being for the most part just beneath the interface in the ZnCdS.⁽⁶⁾ Concentrations of Zn and Cd in the Cu_2S have not yet been conclusively determined as functions of base composition, but do appear to be less than about 10^{20} cm^{-3} (i.e. less than about 0.2 atomic percent). On the other hand, large amounts of excess Zn

have been detected just below the interface for thin film, powder and single crystal ZnCdS base material. Typical values are given in Table 1.

Table 1. Zn/Cd mass ratios for three pertinent samples (discussed in text), for three types of ZnCdS base material

Sample \ ZnCdS Type	Thin Film	Powder	Single Crystal
Base Material	0.162	0.121	0.063
Cu ⁺ Solution	0.093	0.096	0.048
Post HCl Etch	1.52	0.296	0.360

Analyses of the type shown in Table 1 are discussed in greater detail in reference 6. The "Cu⁺ solution" is the aqueous ion-exchange solution, and the "post HCl etch" is a brief etch of the ZnCdS surface following removal of the Cu₂S layer.

The trend of Table 1 has been evident for all samples measured. The ZnCdS region within about 0.2 μ m below the Cu₂S-ZnCdS interface contains an excess amount of Zn.

The model proposed below is based on the existence of excess Zn under the metallurgical interface, and upon the likely anisotropy of this zinc accumulation with crystallographic direction.⁽⁷⁾ The latter effect is expected to result in lateral composition inhomogeneities along a non-planar interface. The objectives of this work are to model the photoresponse of such a laterally graded junction, and to check agreement between results of the model and experimental photoresponse values.

THE MODEL

We have no information related to the exact form of lateral gradients of Zn composition at the interface. Therefore, the geometrical model is somewhat arbitrary. We have chosen a hemispherical model, as shown in Figure 1, for two major reasons: 1) the hemisphere depicts a grain or nodule for a polycrystalline thin film, which is the type of ZnCdS in which we are most interested for photovoltaic applications; 2) a crystallographic anisotropy will exist at the interface, which is required for the proposed lateral composition gradient to occur.

In this model, the Cu_2S thickness is assumed to vary as $\cos \theta$ (Fig. 1). Accumulation of Zn under the interface is assumed to increase with Cu_2S thickness as

$$x(r) = x_{\text{SUB}} (1 + K_2 t^n) \quad (1)$$

where $x(r)$ = atomic fraction of Zn as function of radial distance r ,

x_{SUB} = fraction of Zn in base (base composition)

t = Cu_2S thickness, which is also a function of r

K_2, n = constants

The space charge region is assumed to have a constant value of $0.15 \mu\text{m}$, which is a nominal value resulting from illuminated capacitance data. (Specific results depend on the width of space charge used, although the general trends and resulting conclusions will be similar.)

The hemispherical nodule can be broken down into a large number of infinitesimal "microdiodes." Each microdiode is assumed to have the

Fig. 1. Hemispherical model used in the analysis.

same photocurrent capability, with the amount of photocurrent actually collected depending on the interface collection efficiency $I(x)$ of a particular microdiode. That is

$$J_{SC} = J_{SCO} I(x) \quad (2)$$

where J_{SCO} is a constant and $I(x)$ can be broken down as follows

$$I(x) = F(x)T(x) \quad (3)$$

where $F(x)$ is the interface collection factor $\mu E / (\mu E + S_I)$ and $T(x)$ is a transmission factor. Here x is the Zn fraction, μ is electron mobility, E is electric field and S_I is the interface recombination velocity, all at a particular location r . All of the above parameters (μ , E , S_I and T) are functions of $x(r)$.

The factors $F(x)$ and $T(x)$ are functions of position r . An integral across the hemispherical nodule gives the total photocurrent. The transmission factor $T(x)$ was computed using the band diagram shown in Figure 2. (This band diagram will also be a function of radial position r).

In these computations, modulation of the current density is assumed to occur only at the interface. Effects of the Cu_2S are neglected.

To facilitate computations, equation 2 was modified to

$$J_{SC} = J_{TE} + J_{SB} + J_{TUN} \quad (4)$$

Fig. 2. Band diagram used for current transmission analysis. Cu_2S region is on the left, and $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ on the right.

where J_{TE} = thermionic emission current density

J_{SB} = current density due to Schottky barrier lowering

J_{TUN} = tunneling current density

These contributions are shown in Figure 2. The energy spike results assuming a conventional Cu_2S/CdS type of band diagram, and as so, will exist in those regions of the junction where $x \gtrsim 0.37$. This is discussed further below. J_{SB} can be included in J_{TE} by a change in the integration limit. Thus the photogenerated current for the hemispherical nodule can be represented as two integrals^(8,9)

$$J_{TE} = A \int_0^R e^{-BV(r)} e^{C\sqrt{V_d(r)}} F(r) 2\pi r dr \quad (5)$$

and

$$J_{TUN} = D \int_0^R \int_0^{g(r)} y e^{-Cy^2} e^{-f(y,r)} F(r) 2\pi r dy dr \quad (6)$$

where R is nodule radius, $V(r)$ is the potential spike height determined by the electron affinity difference, $V_d(r)$ is diffusion potential, $g(r)$ is effective spike height, y is the normal component of electron momentum, $F(r)$ is the interface collection factor, A, B, C, D, G are constants at fixed temperature, and $e^{-f(y,r)}$ is a tunneling coefficient. The above integrals were evaluated using numerical values for parameters taken from the literature.^(7,9-11)

RESULTS

Normalized current density for microdiodes as a function of Zn content (x) is shown in Figure 3. The thermionic and tunneling contributions to the total are shown for the barrier reduced by Schottky lowering (solid lines) and without Schottky lowering (dashed lines). It is seen that the current is determined almost exclusively by thermionic emission over the barrier. The microdiode current remains constant until a potential spike appears, as shown in Fig. 2, at about 37% Zn composition. If a macroscopic $\text{Cu}_2\text{S}/\text{ZnCdS}$ solar cell had a uniform interface, it would thus be anticipated that current density should not start to decrease until Zn content of the base exceeded about 37%. The thermionic (and total) current decreases rapidly as shown, since it has been assumed that photogenerated electrons are thermalized when they reach the interface. The electron distribution maximum (in the Cu_2S conduction band) is then located $kT/2$ above the band edge, resulting in the rapid drop in transmission across the interface as soon as the spike appears.

The "macrodiode" current is that produced by the hemispherical nodule, and is found by integrating the microdiode current (equations 4-6). This current (Figure 4) would be that produced by the solar cell, which can be viewed as an assemblage of hemispherical nodules.

The predicted decrease in current density is compared to several experimental values,^(4,12,13) and shows the same general form. For the J_{SC} resulting from the model the following comments can be made. The flat region up to about 7% Zn is because, for the parameters used, a potential spike does not exist anywhere at the junction. Between

Fig. 3. Dependence of normalized current density for infinitesimal cell region ("microdiode") on zinc content below the interface.

Fig. 4. Dependence of normalized current density on base Zn content for entire hemispherical region ("macrodiode"). Delaware (IEC, ref. 12, 13) and IIT (ref. 4) results are shown for comparison.

7 and 37%, a spike exists across an increasing fraction of the junction, and for Zn content above 37% the spike exists across the entire interfacial region. Above base compositions of roughly 45% Zn, essentially no current should cross the junction. This result will depend on parameters (K_2 , M and materials parameters) chosen for the model, but the basic result will be the same.

The V_{OC} generated by the array of microdiodes was found by a summation over diodes, assuming an ideal diode for each element. For this initial set of calculations cross-coupling between diodes was ignored. V_{OC} predicted by the model, and experimental values, are shown in Figure 5. (The dashed line represents computed values normalized to constant current density.) Even though computed values are on the average higher, the general trend is as expected. (Experimental values are for Cu_2S formed by aqueous ion-exchange, as pertains to the model.)

Current-voltage curves were computed for the microdiode arrays for several compositions, assuming ideal diodes, and neglecting series and shunt resistances (Figure 6). These curves are similar to experimental ones, except for the first quadrant, which for the real cell exhibits a larger effective series resistance for the higher Zn compositions ($\geq 20\%$).

A voltage-dependence is seen in J for low voltages, especially for higher Zn content. This is attributed to a lowering of the potential barrier (Schottky effect) as the voltage goes toward and into reverse bias. This effect is also seen in actual cells for $Zn \gtrsim 20\%$. The uneven spacings of the J_{SC} values for the five cases shown in Fig. 6 can be deduced from the general shape of the curve shown in Fig. 4.

Fig. 5. Computed V_{OC} values (solid) and corrected for current density (dashed) as compared to experimental values (references 4, 12 13) for macrodiode.

Fig. 6. Computed J-V curves for several Zn compositions of base.

SUMMARY AND CONCLUSIONS

A model has been presented for the $\text{Cu}_2\text{S}/\text{Zn}_x\text{Cd}_{1-x}\text{S}$ heterojunction, based on a laterally graded composition in the base material at the interface. Due to the enhanced Zn content of this region, a potential energy spike that varies laterally in magnitude controls the transmission of current across the junction. Current density for junctions formed by aqueous ion-exchange is expected to decrease monotonically for base compositions between 7% and 37% Zn ($\text{Zn}_{0.07}\text{Cd}_{0.93}\text{S}$ to $\text{Zn}_{0.37}\text{Cd}_{0.63}\text{S}$) and to be essentially zero for $x \gtrsim 45\%$. The dependences of J_{SC} , V_{OC} and J-V characteristics on Zn content of the base material are in substantial agreement with experimental measurements.

ACKNOWLEDGEMENTS

We appreciate the assistance of Judy Alls and Marilyn Grender for assisting with junction composition measurements.

REFERENCES

1. W. Palz et al., Proc. 10th Photovoltaic Specialists Conference, Palo Alto, CA (IEEE, New York, 1973).
2. L. C. Burton and T. L. Hench, Appl. Phys. Lett., 29, 612 (1976).
3. T. M. Peterson, Ph.D. Thesis, Lawrence Berkeley Laboratory, University of California at Berkeley, 1975.
4. S. R. Das et al., Sol. St. Elec. 22, 533 (1979).
5. L. C. Burton, Solar Cells, 1, 159 (1980).
6. L. C. Burton, Appl. Phys. Lett. 35, 780 (1979).
7. L. R. Shiozawa et al., Rep. ARL 69-0155 (Clevite Final Report), Clevite Corporation, Cleveland, OH (1969).
8. S. M. Sze, Physics of Semiconductor Devices, Wiley (1969).
9. A. G. Milner and D. L. Fenchel, Heterojunctions and Metal-Semiconductor Junctions, Academic Press (1972).
10. L. C. Burton, et al., J. Elec. Mater., 7, 159 (1978).
11. A. Rothwarf, Techn. Rep. 72-03478 76/1, Institute of Energy Conversion, University of Delaware (1976).
12. Prog. Rep. XR-9-8063-1, Institute of Energy Conversion, University of Delaware, p. 17 (1977).
13. L. C. Burton et al., Proc. 12th IEEE Photovoltaic Specialists Conference, Baton Rouge, LA (IEEE, New York, 1976).