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**EMERGING MATERIALS SYSTEMS FOR SOLAR CELL
APPLICATIONS— Cu_{2-x}Se**

Final Report, May 1, 1979—April 30, 1980

By
L. F. Buldhaupt
R. A. Mickelsen
J. M. Stewart
W. S. Chen

April 1980

Work Performed Under Contract No. AC04-79ET23005

Boeing Aerospace Company
Seattle, Washington

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Solar Energy

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FINAL REPORT

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L.F. Buldhaupt, Program Manager
R.A. Mickelsen, Principal Investigator
J.M. Stewart
W.S. Chen

Boeing Aerospace Company
P.O. Box 3999 M/S 88-43
Seattle, Washington 98124

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A total of 16 solar cells was fabricated in the first quarter. Half of these had diffused junctions and half had ion-implanted junctions. In each group of eight, six were made on Wacker "Silso" polycrystalline substrates and two on "control" single-crystal wafers. The solar-cell parameters were measured for all cells.		

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1.0 SUMMARY

The major results from this research program can be summarized as follows:

1) Film Formation Process

A process for forming single phase, face centered cubic structure Cu_{2-x}Se thin films has been developed. This vacuum deposition process utilizes two separate, individually controlled vapor sources (Cu and Se) to produce the binary semiconductor films. The technique has been found to be reproducible and capable of large area deposits with good uniformity across the substrate. The Cu_{2-x}Se films can be formed at substrate temperatures in the range of 150°C to 275°C . At the higher substrate temperatures, the film composition becomes less sensitive to the Se deposition rate (once this rate is above a threshold value). CdS films of low resistivity can also be formed by the coevaporation of CdS with In.

2) Cu_{2-x}Se Film Properties

The structural, optical, and electrical properties of the Cu_{2-x}Se thin films produced by the two vapor source process have been analyzed. X-ray diffraction has indicated that the films are of single phase, face centered cubic structure. The film grain size is on the order of one micron. The composition of the films has been determined to a high degree of accuracy by coulometric analysis.

Optical absorption versus wavelength measurements have been made on the deposited films and show an indirect band gap of 1.4eV and a direct band gap of 2.2eV.

Hall and conductivity measurements indicate Cu_{2-x}Se is p-type with a hole mobility of $10 \text{ cm}^2/\text{V-sec}$ and $2 \times 10^{21} \text{ holes/cm}^3$ for the stoichiometric index "x" equal to 0.2. Reproducibility of the electrical properties was found to be satisfactory for a fixed set of deposition conditions.

3) CdS/ Cu_{2-x}Se Device Formation and Study

During the latter stages of this program, fabrication of complete thin film cells was initiated. When these 1 cm^2 cells were tested under simulated 100 mW/cm^2 illumination, they exhibited an open-circuit voltage of 400mv and a short circuit current of 4ma. Several factors which are degrading cell performance have been identified.

Theoretical estimates have been made for the efficiency of the $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ cell. Both front and back wall design cells indicate that efficiencies greater than 10% are possible.

2.0 INTRODUCTION

This Final Report described the results of a 12-month research program to investigate copper selenide (Cu_{2-x}Se) thin films as an inorganic semiconductor material having considerable potential for mass produced, low cost, high efficiency photovoltaic solar cells. The report summarizes the information contained in the first three Quarterly Reports and presents the experimental results obtained during the Fourth Quarter. This initial research program is regarded as the first phase of the necessary technical effort leading to the development of the low cost thin film arrays and is oriented towards achieving the DoE goals of: (1) developing a thin film photovoltaic device fabrication technology capable of 10% conversion efficiency, and (2) demonstrating feasibility of large scale production at a cost of approximately \$0.30/watt.

Cu_{2-x}Se has a number of characteristics that give it excellent potential for yielding a 10% efficient solar cell. Band gap measurements by previous investigators have found values in the range of 1.1 to 1.29eV^(1,2). Measurements by this laboratory have given values of 1.4eV for the indirect band gap and 2.2eV for the direct band gap. The f.c.c. structure obtained has a lattice constant of $a = 5.76\text{\AA}$. This will then give a very small lattice mismatch with the N-type CdS layer. With the use of N-type CdS, consideration of the electron affinity of the materials shows there will be no detrimental interfacial spike in the conduction band between the two materials.

The specific objectives of this contract, which were satisfactorily achieved, can be divided into the following major research tasks:

- 1) Develop and characterize the Cu_{2-x}Se thin film deposition process.
- 2) Characterize the electrical, optical, and structural properties of the Cu_{2-x}Se films.
- 3) Fabricate simple $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ cell structures.

3.0 TECHNICAL DISCUSSION

3.1 Copper Selenide Film Deposition Apparatus

The vacuum system for the deposition of the Cu_{2-x}Se films is a conventional 24 inch, stainless steel bell jar vacuum chamber with a liquid nitrogen trapped oil diffusion pump. In addition the system has a liquid nitrogen shroud which enables the system to maintain a base pressure of 10^{-7} torr and a pressure of 8×10^{-6} torr during deposition. A mask changing fixture is also contained within the system for multiple deposits.

The semiconductor films are deposited onto 0211 Corning glass substrates. Initial attempts at depositing Cu_{2-x}Se films on glass substrates gave very poor results. The films produced gave wide variations in resistivity across the film and visually the films had a very nonuniform appearance. It is believed that this was due to the poor thermal conductivity of the glass substrate resulting in temperature gradients across the film. This problem has been solved by mechanically bonding the glass substrate to a ceramic substrate that has improved heat transfer capability. In addition, the substrate is preheated to the appropriate temperature at least 5 minutes before the deposition begins.

The substrate assembly is heated by passing a current through a carbon cloth. It has been determined from the CuInSe_2 research effort that the carbon heater will give localized but uniform heating.⁽³⁾ On the back side of the carbon cloth another ceramic substrate is affixed with a thermocouple bonded to the ceramic material. A fixed substrate temperature is maintained with a Honeywell Electronik 18 Controller. A schematic diagram of the substrate and heater is shown in Figure 3.1-1.

The deposition procedure uses two separate, individually controlled vapor sources for the Cu and Se materials. It is believed that this method gives greater flexibility and controllability not only for this small scale research effort, but is readily adaptable to large scale high production efforts. The Cu source is a standard tungsten boat coated with an Al_2O_3 barrier. The Se is evaporated from a "ring" source-mounted concentrically to the Cu source. The Se ring source is made from Cu with multiple plated coatings of Au and Ni to minimize any chance of reaction of Se with the Cu boat.

FIGURE 3.1-1 SUBSTRATE - HEATER SCHEMATIC

Two quartz crystal microbalances are used to separately monitor the Cu and Se materials. With the use of appropriate shielding, each microbalance is in "line of sight" with only one material at all times. It was anticipated that re-evaporation of the high vapor pressure material Se could give erroneous readings on the Cu sensor, however, experimental results indicate this is not a problem. With the Se source on at rates comparable to actual deposition conditions (heated substrate), Se was not detected on the Cu sensor (the Cu source was turned off). A schematic of the quartz crystal microbalance, deposition sources, substrate and shutter arrangement appears in Figure 3.1-2.

For analysis purposes each separate deposition on the Corning 0211 glass substrate has four distinct sections, with each section of suitable size and thickness for the particular analysis to be performed. For a given deposit, one section is approximately $1000\text{\AA}$ thick. This is used for optical absorption measurements to determine the band gap. A second section is removed from the substrate and mounted on a nickel screen for diffraction analysis on the electron microscope. A third section of the film is used for Hall and resistivity measurements. Finally, a fourth section is used for Coulometry measurements to determine the film composition. The layout of the substrate deposit is shown in Figure 3.1-3.

3.2 Film Characterization

3.2.1 General Characteristics

According to the literature⁽⁴⁾, two stable phases (α, β) of Cu_{2-x}Se exist at room temperature depending on the stoichiometric parameter "x". The α -phase exists at room temperature and has a hexagonal lattice with $a = 7.07\text{\AA}$ and $c = 6.68\text{\AA}$ ⁽⁵⁾. The β -phase⁽⁴⁾ occurs for $0.20 \leq x \leq 0.25$ and has f.c.c. structure with a lattice constant of $5.7605\text{\AA}$.

Our cubic phase thin films have an x value in the range of 0.15 to 0.26.

Some of our very thin films ($\sim 700\text{\AA}$ thickness) show degradation over a 5-day period. It is probable the films are changing from cubic to hexagonal structure⁽⁶⁾. Heat treatment at 100°C in a reducing atmosphere restores the appearance of these films. No extensive work has been done yet on this characteristic. No degradation has been observed to date on films greater than $700\text{\AA}$ in thickness.

FIGURE 3.1-2 SCHEMATIC OF VACUUM DEPOSITION APPARTUS FOR Cu_{2-x}Se

FIGURE 3.1-3 SCHEMATIC LAYOUT OF SUBSTRATE

On actual film preparation it has become clear that there is significant reevaporation of Se after the Cu_{2-x}Se film has been deposited, if the substrate temperature is 170°C or greater. Hence, the substrate heater is shut off immediately after the deposit to prevent the reevaporation of Se.

The Cu deposition rate must be of the order of $14\text{\AA}/\text{sec}$ or greater at the substrate to avoid the formation of porous films. A temperature of 170°C at the substrate surface is necessary in order to produce grain sizes of order one micron. The highly desirable cubic phase of Cu_{2-x}Se is produced with deposition rates of at least $14\text{\AA}/\text{sec}$ of Cu and $19\text{\AA}/\text{sec}$ of Se. These deposition rates give a stoichiometric parameter "x" between 0.15 and 0.26.

3.2.2 Film Structural Studies

The Cu_{2-x}Se films were analyzed with the aid of a transmission microscope (JEOC Model 6AS). The standard technique has been to deposit the films onto glass substrates, remove with an HF, water, acetone, glass etchant, and mount on copper grids for transmission electron diffraction (High Resolution) at 100kV. Because extraneous lines were frequently present in the diffraction patterns which appeared to correspond to a hydrated copper silicon fluoride compound, nickel grids have been substituted for the standard copper material.

The electron diffraction data on one film deposited at 170°C with Cu and Se deposition rates adjusted such that the coulometric determined 'x' value was 0.15 are presented in Table 1. With this 'x' value, the literature predicts the existence of the cubic Cu_{2-x}Se phase⁽⁴⁾. In Table 3.2-1, the 'd' values and relative intensities of the first 16 lines in the electron diffraction pattern are listed. The hkl indices for each line (assuming a face centered cubic structure) are also listed along with the values contained in the ASTM index card for Cu_{2-x}Se (Berzelianite, cubic, $a_0 = 5.739\text{\AA}$, card 6-0680). There is seen to be good agreement with the measured lines and the cubic Cu_{2-x}Se material. No extra lines were present with the exception of lines with 'd' values of $1.66\text{\AA}$, $1.29\text{\AA}$, and $0.771\text{\AA}$. However, these three lines correspond to reflections from the (222), (420), and (642) planes, respectively, for a face centered cubic structure. The high sensitivity of the high resolution electron diffraction technique and/or possible preferred orientation effects may be responsible for the detection of these lines in the present case while not being listed on the ASTM card.

TABLE 3.2-1 ELECTRON DIFFRACTION DATA FOR DEPOSITED COPPER SELENIDE FILM

Intensity	Deposited Cu_{2-x}Se Film, run 84, $x = 0.21$		Cubic Cu_{2-x}Se , ASTM		Lattice Parameter (Å)
	'd' Value (Å)	(hkl)	d(Å)	I/I ₁	
M	3.33	111	3.33	90	5.77
W	2.87	002	2.88	10	5.74
S+	2.03	022	2.02	100	5.74
M	1.74	113	1.729	80	5.77
W	1.66	(222)	----	---	5.75
W	1.44	004	1.434	30	5.76
M-	1.32	133	1.317	20	5.75
W-	1.29	(420)	----	---	5.77
M	1.18	224	1.171	40	5.78
W	1.109	115	1.105	20	5.76
W+	1.020	044	1.014	10	5.77
W+	0.973	135	0.969	10	5.76
W-	0.910	026	0.908	20	5.76
W-	0.881	335	0.876	10	5.78
W	0.805	117	0.804	10	5.75
M	0.771	(642)	----	---	5.77

Cu_{2-x}Se 5.76⁰Å Ave.
 CdS 5.85⁰Å

Finally, by using the 'd' and hkl values, the lattice parameter for the deposited cubic material was calculated with the results also displayed in the table. The average value was $5.76\text{\AA}$ which exactly agrees with the parameter for Cu_{2-x}Se material with an 'x' value of 0.15⁽⁶⁾.

3.2.3 Film Composition Measurement

An apparatus has been designed and built for Coulometric measurements^(7,8). This apparatus was used to determine the composition of Cu_{2-x}Se to a high degree of accuracy. Coulometric methods of analysis are based on the exact measurement of the quantity of current that passes through a solution during an electrochemical reaction. The substance to be measured may be oxidized or reduced or may react quantitatively in solution with a single product of electrolysis. The requirement of Coulometric analysis is that only a single reaction take place for which the electrode reaction used for the determination proceeds with 100 percent current efficiency. The reactant is generated in controlled amounts within the electrolytic cell. The amount of reactant formed between the beginning and end of the process is proportional to the net charge, Q, transferred. For a constant current process, where i is current and t is time, $Q = i t$ and only the reaction time need be measured.

For the compound Cu_{2-x}Se under consideration, the reduction reaction takes place in two steps:

The completion of each of these steps is signalled by a change in the voltage between a Calomel reference electrode and the sample. Deviations from stoichiometry are then determined by calculating "x". The number of coulombs Q to complete the first (Q_1) and second (Q_2) reduction reactions above then determine the value of "x" by

$$x = \frac{2Q_1}{Q_1 + Q_2}$$

A schematic of the apparatus is shown in Figure 3.2-1. Actual data taken for a cubic structure film with x determined by coulometry to be 0.15 is shown in Figure 3.2-2.

FIGURE 3.2-1 COULOMETRIC APPARATUS

FIGURE 3.2-2 SAMPLE OF CONDOMETRIC DATA

A series of Cu_{2-x}Se deposits were made and analyzed by the coulometric technique to determine the stoichiometric parameter "x". A plot of "x" vs. atomic percent Se (Figure 3.2-3) has shown that for a substrate temperature of 170°C , the value of "x" lies in the range of 0.22 to 0.26. The consequences of this are that one need not rely on careful deposition rate control to fix the ratio of Cu to Se. The substrate temperature will be the parameter controlling the film composition.

3.2.4 Electrical Properties

The film electrical properties (Hall mobilities, carrier concentration) have been measured with the aid of a Hall⁽⁹⁻¹²⁾ apparatus, shown in Figure 3.2-4. For this measurement, the electrodes are attached to the four corners of the Cu_{2-x}Se film by indium. For $\text{Cu}_{1.8}\text{Se}$ the hole mobility is $10 \text{ cm}^2/\text{V-sec}$ and the hole concentration is $2 \times 10^{21} \text{ holes/cm}^3$.

3.2.5 Band Gap Measurements

The Cary 14 spectrophotometer was used to measure the relative optical transmission as a function of wavelength. With the proper deposition conditions to produce cubic material, a typical curve of absorption versus wavelength is shown in Figure 3.2-5a. The films are seen to be quite transparent through the visible spectrum. The absorption at the longer wavelengths is attributed to the free carrier absorption.

The free carrier absorption is given by⁽¹³⁾

$$A \propto \lambda^2$$

where A is the absorbance. A plot of $A^{1/2}$ vs. λ in the long wavelength region is a straight line. This line is then subtracted from the curve in Figure 3.2-5a to remove the effect of the free carrier absorption. The results are shown in Figure 3.2-5b.

The band gap width can be determined with the aid of the relations

$$A \propto (\hbar\omega - E_g)^{1/2}$$

for the direct band gap and

$$0.01 \quad A \propto (\hbar\omega - E_g)^2$$

for the indirect band gap. One then plots A^2 vs. $\hbar\omega$ and $A^{1/2}$ vs. $\hbar\omega$ to determine the energy for the direct and indirect band gap. These results are shown in Figure 3.2-6. The values obtained are:

$$E_{g_{\text{direct}}} = 2.2\text{eV}$$

$$E_{g_{\text{indirect}}} = 1.4\text{eV}$$

FIGURE 3.2-3. Stoichiometric Index "x" vs. Atomic Percent Se.

FIGURE 3.2-4 HALL APPARATUS

FIGURE 3.2-5 Absorbance of $\text{Cu}_{1.83}\text{Se}$ as a Function of Wavelength
(a) As Measured, (b) After Subtracting the Free Carrier Absorption

FIGURE 3.2-6 Absorbance Data of $\text{Cu}_{1.83}\text{Se}$ Indicating Direct and Indirect Transitions

These values are obtained for the stoichiometric index in the range $0.17 \leq x \leq 0.25$. The values for a Cu_2Se film by going through the same process as above yield;

$$E_{g_{\text{direct}}} = 2.2\text{eV}$$

$$E_{g_{\text{indirect}}} = 1\text{eV.}$$

3.3 Device Development

3.3.1 Cell Fabrication

Two basic cell structures, front and back wall, were designed and investigated. A cross section of these devices is shown in Figure 3.3-1. The back wall cell fabrication will be described in some detail as the majority of effort was expended on this configuration.

The first cell layer consists of a Mo/Au grid on the Corning 0211, 2"x2" glass substrate. The film thicknesses were $3000\text{\AA}$ and $5000\text{\AA}$, respectively. The grid consists of ten equally spaced lines of 0.002" in width and is shown in Figure 3.3-2a.

A mask change is next made without breaking vacuum for the deposition of the CdS layer. The mask for this layer is shown in Figure 3.3-2b. At a substrate temperature of 185°C , the CdS is evaporated with or without In. When CdS is coevaporated with In, it is deposited with one atomic percent In at a deposition rate of $125\text{\AA}/\text{sec}$. The resistivity of undoped CdS is beyond the four-point probe range. The resistivity of In doped CdS is approximately $0.01\Omega\text{cm}$. The CdS is deposited to a total thickness of $10\mu\text{m}$ to avoid pinhole problems.

A mask change is again made without breaking vacuum for the deposition of Cu_{2-x}Se . The configuration of this layer is $(4)\text{-}1\text{cm}^2$ films of approximately $5\mu\text{m}$ thickness. This layer is shown in Figure 3.3-2c. The final layer consists of $5000\text{\AA}$ of Au shown in Figure 3.3-2d. For test purposes the glass substrate is scored and separated into individual cells.

A significant number of cells made to date appears to have a shorting problem between the Mo/Au grid and the Cu_{2-x}Se layer due to pinholes in the CdS layer. These defects are probably caused by dust particles on the glass substrate as well as the debris from the shields and walls in the evaporation chamber before or during deposition. Improvement of the final substrate rinse procedure and special manipulation of the substrate in the chamber before deposition has been made to avoid the pinhole problems.

(a) Back Wall

(b) Front Wall

FIGURE 3.3-1 Cell Structure

(a) Base metallization grid

(b) CdS film

(c) Cu_{2-x}Se film

(d) Au top electrode

FIGURE 3.3-2 Solar Cell Test Structure, 1 cm^2 Area Cell

3.3.2 Theoretical Cell Performance

A preliminary theoretical study to estimate the achievable efficiency of the thin film $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ cell has been made. Results show that efficiencies of more than 10% can be achieved for both front wall and back wall type cells.

Cu_{2-x}Se crystal ($x \approx 0.2$) has a cubic structure of lattice constant $5.76\text{\AA}$ and is a degenerate P-type semiconductor with a band gap energy of 1.3-1.4eV. When it forms a heterojunction with CdS ($E_g = 2.44\text{eV}$, $\sqrt{2}a_{\text{CdS}} = 5.85\text{\AA}$), the small lattice mismatch (1.5%) and favorable electron affinity difference ($\chi_{\text{CdS}} - \chi_{\text{Cu}_{2-x}\text{Se}} \approx 0.15\text{eV}$) should give a junction with few interfacial states and no interfacial conduction band potential spike to impede the electron flow. The band diagram of the heterojunction is shown in Figure 3.3-3.

The $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ heterojunction is similar to the $\text{Cu}_2\text{S}/\text{CdS}$ junction. The diode transport mechanism of the $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ junction is therefore anticipated to be the same as $\text{Cu}_2\text{S}/\text{CdS}$ junction, i.e., dominated by recombination through interface states created by the lattice mismatch.⁽¹⁴⁾ The dark current due to this recombination mechanism can be given as⁽¹⁴⁾

$$J = qS_I N_{C2} \exp - (E_{g1} - \Delta x - S)/kT \exp\left(\frac{qV}{kT}\right) \\ = J_0 \exp\left(\frac{qV}{kT}\right)$$

where S_I is the interface recombination velocity and N_{C2} is the effective density of states of the CdS conduction band. The interface recombination velocity is approximately

$$S_I = V_{th} \sigma_n N_I \quad (2)$$

where V_{th} is the thermal velocity (10^7cm/sec), N_I is the surface concentration of the interface states, and σ_n is the electron capture cross section for such states ($10^{-14} - 10^{-15} \text{cm}^2$).⁽¹⁵⁾ The interface states can be considered as edge dislocations due to the lattice mismatch. Their surface concentration can be estimated as⁽¹⁵⁾,

$$N_I = \frac{1}{a_1^2} - \frac{1}{a_2^2} \approx \frac{2}{a_1 a_2} \frac{\Delta a}{a} \quad (3)$$

For the materials under consideration, we have

$$a_1 = a_{\text{Cu}_{2-x}\text{Se}} = 5.76\text{\AA} \quad a_2 = \sqrt{2} a_{\text{CdS}} = 5.85\text{\AA}$$

FIGURE 3.3-3 Band Diagram of $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ Heterojunction

which gives $N_I = 9.2 \times 10^{12} \text{ cm}^{-2}$ and $S_I = 9.2 \times 10^4 \text{ to } 9.2 \times 10^5 \text{ cm/sec}$.

Since $N_{C2} \approx 2 \times 10^{18} \text{ cm}^{-3}$, we have, at 300°K ,

$$\begin{aligned} J_0 &= qN_{C2}S_I \exp\left[-(E_{g1} - \Delta x - S)/kT\right] \\ &= 3.28 \times 10^{-14} - 3.28 \times 10^{-13} \text{ A/cm}^2 \end{aligned} \quad (4)$$

The value of J_0 is smaller than the calculated value for the $\text{Cu}_2\text{S/CdS}$ cell. This is due to a better lattice match (smaller S_I) and the difference of the electron affinities (small Δx) between the Cu_{2-x}Se and CdS .

The ideal light generated current (quantum efficiency = 1) at the AM1 condition can be estimated from the band gap energies of CdS and the Cu_{2-x}Se material. For the front wall structure, the light illuminates through the Cu_{2-x}Se side. The ideal light-generated current (I_L) is approximately 35 mA/cm^2 .⁽¹⁶⁾ For the back wall cell, the light is through the CdS side. There is no response to the short wavelength light with photon energies greater than 2.44 eV due to the CdS absorption (window effect). The estimated current (I_L) is 28 mA/cm^2 .⁽¹⁶⁾

The quantum collection efficiency of a thin film polycrystalline cell depends upon careful design and processes (film thickness, backside reflector, light trapping, antireflection coating, junction field, etc.) as well as material properties (grain size, minority carrier lifetime, diffusion length, etc.). From the experience on the development of thin film front wall $\text{Cu}_2\text{S/CdS}$ cells where the best achieved quantum collection efficiency is 0.7 ,⁽¹⁷⁾ we believe that with careful design and optimization, this value (0.7) can also be achieved in the front wall $\text{Cu}_{2-x}\text{Se/CdS}$ cell. The back wall cell reduces the surface recombination because the absorption is at the junction. The quantum collection efficiency of this type of cell should be higher than the front wall cell. The achievable quantum efficiency should be in the range of $0.7 - 0.8$.

From the ideal light generated current and the achievable quantum efficiency, the realistic light generated current can be estimated as

$$\begin{aligned} I_L &= 25 \text{ mA/cm}^2 \quad \text{front wall cell} \\ I_L &= 20-22 \text{ mA/cm}^2 \quad \text{back wall cell.} \end{aligned} \quad (5)$$

The achievable open circuit voltage, therefore, can be estimated from

$$\begin{aligned} V_{oc} &= \frac{kT}{q} \ln \frac{J_L}{J_0} \\ &= E_{g1} - \Delta x - S + \frac{kT}{q} \ln \frac{J_L}{qN_{C2}S_I} \end{aligned} \quad (6)$$

With values of J_L (Eqn. 5) and J_0 (Eqn. 4), we have

$$V_{oc} = 0.64 - 0.69V \text{ for front wall cell} \\ = 0.63 - 0.68V \text{ for back wall cell.}$$

Mitchell has calculated the ideal fill factor as a function of J_L/J_0 .⁽¹⁸⁾ From his theory, the fill factor of the $Cu_{2-x}Se/CdS$ cell is 0.84. In reality, however, the fill factor is reduced due to series and shunt resistance as well as the voltage dependence of the collection efficiency. Therefore, the most probable achievable AM1 performance of the $Cu_{2-x}Se/CdS$ cell is:

for front wall cell	$V_{oc} = 0.64V$
	$J_L = 24mA/cm^2$
	F.F. = 0.71 (achieved in Cu_2S/CdS cell)
	$\eta = 10.9\%$
for back wall cell	$V_{oc} = 0.63V$
	$J_L = 22mA/cm^2$
	F.F. = 0.75
	$\eta = 10.4\%$

In conclusion, with a preliminary analysis and past experiences in developing Cu_2S/CdS and $CuInSe_2/CdS$ cells, we estimate the 10% efficiency of the thin film polycrystalline $Cu_{2-x}Se/CdS$ cell of either front wall or back wall type can be attained.

3.3.3 Cell Performance

Fabrication of both front wall and back wall cells were initiated during the third quarter. We have had problems in common with other groups⁽¹⁹⁾ in that CdS deposited on either predeposited Al or freshly evaporated Al films forms non-ohmic and high resistance contacts. However, a response can be measured from our cells by soldering In onto the CdS films. As-deposited cells are usually quite leaky. A short time (1-5 min.) 200°C annealing in H_2/Ar ambient is needed for the cell to show diode characteristics and photovoltaic response. Under the simulated AM1 illumination (ELH Lamp, calibrated by a standard Si cell) cells with open circuit voltages of 0.2-0.37 volt and short circuit currents of 20-45 μA have been observed. A typical cell I-V characteristic is shown in Figure 3.3-4. In the dark the cell shows a high resistance. Under illumination, a cross over effect is observed. The contact to the CdS is In soldered around the $Cu_{2-x}Se$ film instead of the Al grids as shown in the insert of Figure 3.3-4. By using a light spot to check the response

FIGURE 3.3-4 Dark and Light I-V Characteristics of a Typical Earlier Cell

across the 1 cm^2 area, it was found that only the edge of the Cu_{2-x}Se near the In contact has response to the light. The low short circuit current may be due to a large portion of the cell not responding to the illumination.

In the later part of this program, Mo/Au has been used as a base grid contact to the CdS. Although the Mo/Au greatly improves the contact property, occasionally, non-ohmic or high resistance contacts were still formed. Performance of the improved cells made of pinhole free, non-In doped CdS film has greatly improved compared to the earlier cells. Open circuit voltage and short circuit current were in the range of 0.3-0.45 volt and 2-4.5mA/cm², respectively. A typical cell characteristic is shown in Figure 3.3-5. The cell has an Au grid in contact with the Cu_{2-x}Se layer and was tested under simulated AM1 illumination. Cell performance of $V_{oc} = 0.4\text{V}$, $I_{sc} = 3.5\text{mA/cm}^2$, F.F. = 0.36, and $\eta = 0.51\%$ has been achieved.

The cell performance, though gradually improving, is still far below the theoretical prediction. The open circuit voltage can be improved by reducing the CdS resistivity. The short circuit current can be increased by optimizing the stoichiometry of the Cu_{2-x}Se film. The poor fill factor due to the high series resistance may be improved by a combination of lower CdS resistivity and improving the metal/CdS contact.

Preliminary results show that cells made with In-doped CdS are quite leaky or shorted. A long time (>10 min.) annealing is needed for the cell to show a reasonable diode characteristics. Photoresponse of such cells are unstable, degrading during the measurements. Further investigation by controlling the In doping as well as the composition of the Cu_{2-x}Se is needed.

FIGURE 3.3-5 Dark and Light I-V Characteristics of Improved Cell

4.0 REMAINING PROBLEMS AND RECOMMENDATIONS

The two-source evaporation has been demonstrated to be capable of producing single-phase cubic structure Cu_{2-x}Se films of high mobility, low resistive, and large crystalline grain sizes. The Cu_{2-x}Se film has been proved to be compatible with CdS to form a heterojunction with photovoltaic response. Theoretical studies show that cells with efficiencies over 10% should be attainable. As in any research study, however, a number of problem areas were encountered and have been defined for resolution in the future development of the cell. These include the following:

a. Ohmic Contact to CdS

Evaporation of CdS on either predeposited or freshly evaporated Al metallized substrates has proved to form a non-ohmic and high resistive contact. Substrates coated with Mo/Au make a better contact to the CdS, but the results are not always reproducible. Metal contacts like Cu/Zn or ITO should be investigated.

b. CdS Resistivity Control

The high resistivity CdS not only gives a low barrier junction (hence low open circuit voltage) but also introduces high series resistance. Coevaporated In with CdS does give low resistivity CdS. The influence of the In doping to the heterojunction as well as the photovoltaic response should be investigated. Using a hydrogen bake to control the CdS resistivity, while not as compatible to the in situ process of making the Cu_{2-x}Se cells, should also be investigated.

c. Composition of Cu_{2-x}Se

Cu_{2-x}Se ($x \approx 0.2$) has a cubic structure of lattice constant $5.76\text{\AA}$ and is a degenerate p-type semiconductor with an indirect band gap energy of 1.4eV. When it forms a heterojunction with CdS ($E_g = 2.44\text{eV}$, $\sqrt{2}a = 5.85\text{\AA}$), it should have a good photovoltaic response. Cu_{2-x}Se crystalline film of other compositions with $0 \leq x \leq 0.2$ should be investigated. The lattice mismatch between Cu_{2-x}Se ($0 \leq x \leq 0.2$) and CdS may be increased, but the optical properties as well as the degree of degeneracy of the Cu_{2-x}Se also changes. An optimized composition may be found as a compromise between the lattice mismatch and the optical and electrical properties.

d. Finally, the detailed analysis and characterization of the thin-film $\text{Cu}_{2-x}\text{Se}/\text{CdS}$ cells should be initiated in order to understand the basic cell mechanisms. Cell modeling should accompany this analysis for the purpose of determining design limits of cell configurations and defining directions for cell performance improvements.

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