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INVESTIGATION OF SOLAR CELLS
BASED ON Cu_2O ,

Progress Report,
For Period
6/1/80 - 11/30/80

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Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the Solar Energy Research Institute.

PREFACE

The overall objective of this program is to investigate Cu_2O as a candidate material for low cost photovoltaics. The objectives of the proposed effort include: continuation of the development and characterization of controllably doped Cu_2O substrates and evaluation of alternate approaches to thin film growth; development of conductive ZnO films of good optical quality for application in heterojunction devices; development and characterization of greater than 1 cm^2 Cu_2O based Schottky barrier, MIS, or heterojunction solar cell structures with analysis of the mechanisms which control the photocurrent, junction rectification and limit the photovoltaic efficiency; and demonstration of Cu_2O solar cell devices with total areas greater than 1 cm^2 and photovoltaic efficiencies above 6 percent. The most important issue being addressed in the program concerns junction formation. The photocurrent of Cu_2O cells is approaching 9 mA/cm^2 . Open-circuit voltage values typically are in the range of 0.3 to 0.4 volts. To achieve adequate efficiencies, it is necessary to obtain V_{OC} values closer to 1 volt. As a result, emphasis is being placed on fabrication and characterization of cell structures which have the potential to produce such voltages.

SUMMARY

Progress was made in three areas, namely: microstructure of Cu_2O substrates; correlation of Cu_2O microstructure with $\text{Cu}/\text{Cu}_2\text{O}$ cell properties; and in fabrication of $\text{Tl}/\text{Cu}_2\text{O}$ Schottky barriers.

Characterization of Cu_2O substrates with IMMA indicates that Cl is uniformly distributed through grains, Mg precipitates at grain boundaries and Na and Fe precipitates occur throughout the material. It is clear that the presence of Cl results in lower p-type resistivities. Previous photoresponse scans established that grain boundaries are not significantly active concerning minority carrier recombination. I-V analyses of $\text{Cu}/\text{Cu}_2\text{O}$ cells indicate that leakage current components are a result of distributed effects, and not a grain boundary mechanism. It is not yet clear whether the distributed effects are strictly a surface effect, or a result of bulk defects such as Na and Fe precipitates.

$\text{Tl}/\text{Cu}_2\text{O}$ Schottky barrier studies are progressing well. This device structure is being used as a means of determining if a significant built-in voltage can be achieved with a Cu_2O cell. Problems were encountered concerning deposition of thin Tl films. The films tend to agglomerate. Substrates will be cooled to counter the apparent lateral diffusion. V_{oc} values greater than 0.6 volts were obtained with thick film $\text{Tl}/\text{Cu}_2\text{O}$ cells, however. These results suggest an improved built-in potential was achieved.

TABLE OF CONTENTS

	<u>Page</u>
Preface -----	ii
Summary -----	iii
List of Figures -----	v
1.0 INTRODUCTION -----	1
1.1 Basis For Investigating Cu ₂ O -----	1
1.2 Key Technical Issues -----	4
2.0 Cu ₂ O SUBSTRATE FABRICATION -----	5
2.1 Growth and Doping of Cu ₂ O -----	5
2.2 Cu ₂ O Substrate Microstructure -----	5
3.0 N-TYPE SEMICONDUCTOR FILMS -----	12
3.1 ZnS and ZnO -----	12
3.2 Other Materials -----	12
4.0 Cu ₂ O SOLAR CELL STUDIES -----	15
4.1 Cu/Cu ₂ O Device Studies -----	15
4.2 Tl/Cu ₂ O Device Studies -----	18
5.0 FUTURE WORK -----	25
APPENDIX A	
RESEARCH CONTRIBUTORS -----	26
APPENDIX B	
REPORT DISTRIBUTION -----	28

LIST OF FIGURES

	<u>Page</u>
Figure 1. Approach to Growth and Doping of Cu_2O . -----	6
Figure 2. Cu_2O Resistivity vs MgCl_2 Temperature. -----	7
Figure 3. Picture of Cu_2O Substrate With Small Area Cells And Typical I-V Curves. -----	8
Figure 4. Optical Micrographs Cu_2O Substrate Surface Morphology. -----	9
Figure 5. Optical Micrographs Showing Channels in Cu_2O .-----	10
Figure 6. Summary of Pertinent Data For Candidate N-Type Partners In A Cu_2O Heterojunction. -----	13
Figure 7. Summary Of Theory For I-V Characteristics of MIS Structure. -----	16
Figure 8. Electronic and Thermodynamic Considerations Which Indicate $\text{Tl}/\text{Cu}_2\text{O}$ Schottky Barriers Should Be Considered. -----	20
Figure 9. Sheet Resistance of Thallium Films Measured In Situ As Film Is Deposited.-----	22
Figure 10. Optical Micrograph of Thick Thallium Film Showing Effects of Agglomeration. -----	23
Figure 11. Illuminated I-V Characteristics of $\text{Tl}/\text{Cu}_2\text{O}$ Schottky Barriers. -----	24

LIST OF TABLES

Table 1. Properties of Cu_2O . -----	2
Table 2. Theoretical And Practical Efficiencies. -----	3
Table 3. I-V Parameters For $\text{Cu}-\text{Cu}_2\text{O}$ Cells.-----	17
Table 4. Barrier Height And Interfacial Layer Parameters.-----	19

1. INTRODUCTION AND BACKGROUND MATERIAL

The overall objective of this program is to determine the feasibility of Cu_2O as a photovoltaic material. Specific objectives of the proposed effort include: (1) continuation of the development and characterization of controllably doped Cu_2O substrates and evaluation of alternate approaches to thin film growth; (2) development of conductive ZnO films of good optical quality for application in heterojunction devices; (3) development and characterization of greater than 1 cm^2 Cu_2O based Schottky barrier, MIS, or heterojunction solar cell structures with analyses of the mechanisms which control the photocurrent, junction rectification and limit the photovoltaic efficiency; and (4) demonstration of Cu_2O solar cell devices with total areas greater than 1 cm^2 and photovoltaic efficiencies above 6 percent.

In the remainder of this section, brief discussions are given concerning the basis for investigating Cu_2O and key technical issues to be addressed in the program.

1.1 Basis for Investigating Cu_2O

There are three primary reasons for investigating Cu_2O as a potential material for low-cost photovoltaic power generation, namely:

- (i) Theoretical solar cell efficiency;
- (ii) Material abundance;
- (iii) Simple process for semiconductor layer formation.

Some basic properties of Cu_2O are given in Table 1. The band gap is 2.0 eV, which is in the appropriate range for photovoltaics. The material is p-type as-grown. An approach to dope Cu_2O n-type has not been determined.

The maximum power conversion efficiency for Cu_2O is determined by assuming the photocurrent acquires the maximum possible value, and that parasitic current losses are due only to injection of minority carriers across the

Table 1
PROPERTIES OF Cu₂O

Band Gap	2.0 eV (Direct)
Electron Affinity	3.2 eV
Crystal Structure	Simple Cubic
Lattice Constant	4.27 Å
Melting Point	1235°C
Density	6.0 g/cm ³
Thermal Expansion Coefficient	3.5 x 10 ⁻⁶ °C ⁻¹
Conductivity Type	p-type

junction formed either by a homojunction, or a heterojunction. The maximum photocurrent that can be generated by a cell based on Cu₂O is 17.2 mA/cm². If one assumes that current losses are due to injection of minority carriers from one side to the other of a homojunction, or a heterojunction involving a large bandgap, n-type material in conjunction with Cu₂O, then the J₀ -value can be estimated by

$$J_{0i} \approx 10^8 \cdot \exp(-E_g/kT) \text{ A/cm}^2$$

and the maximum AM1 efficiency is calculated to be approximately 22%. If one assumes that current losses are due to a recombination-current mechanism, the associated J₀-value should be on the order of

$$J_{or} \approx \exp(-E_g/2kT)$$

For Cu₂O, J_{or} ≈ 2 x 10⁻¹⁷ A/cm² and the corresponding maximum efficiency is 13%

Investigations of Cu₂O solar cells made to date suggest that a photocurrent of 12 to 14 mA/cm² appears to be a realistic goal. Furthermore, results regarding device quality and J₀ values are adequately encouraging so that a J₀-value of 10⁻¹⁷ A/cm² appears feasible. As a result, a practical efficiency between 8 and 10% constitutes a realistic goal for future Cu₂O research and development. Maximum possible efficiencies for several current loss mechanisms, and projected practical efficiency are given in Table 2.

Table 2
THEORETICAL AND PRACTICAL EFFICIENCIES

J_{PH} (mA/cm ²)	Parasitic Current Mechanism	J_0 (A/cm ²)	n	Efficiency (%)
17.2	Injection	3.9×10^{-26}	1	22
17.2	Recombination	2×10^{-17}	2	13
12.0	MIS or Heterojct. (Several Possible Mechanisms)	10^{-17}	1	10
		10^{-15}	1	8

Copper is one of the most abundant minerals in the earth's crust. Furthermore, the cost of copper is sufficiently low that one finds the contribution to projected cell cost due to raw copper is negligible. The high abundance of copper also allows one to project a power capacity (based on 10% cells) which exceeds that required by the United States by orders of magnitude.

Another very important advantage of Cu₂O as a photovoltaic material concerns material growth. Formation of semiconducting layers will be one of the most costly steps in any low-cost, solar cell fabrication scheme. In the case of Cu₂O, this step may ultimately be very simple. Copper sheet can be oxidized at 1000°C to achieve Cu₂O sheet with grains several millimeters wide. Copper sheet can also be partially oxidized to obtain Cu₂O films with grain sizes several hundred μ m wide.

The parasitic current losses must eventually be reduced such that the corresponding J_0 -value is on the order of 10^{-15} A/cm². Recent advances have been made concerning the reduction of J_0 in Cu₂O cells. GaAs single crystal devices have been fabricated which are characterized by even lower J_0 -values; thus, the required J_0 -values are clearly possible.

1.2 Key Technical Issues

The most important question to be answered concerning Cu_2O is related to junction formation. In particular, can a junction be formed characterized by a built-in potential on the order of 1 volt? The most desirable approach to junction formation would, of course, involve a homojunction. No approach to doping Cu_2O n-type is known. Thus, a heterojunction or MIS structure must be utilized.

Other key issues concern photocurrent and material science related to growth and doping of Cu_2O . The photocurrent issue was effectively addressed during the last contract period. A value of 8.5 mA/cm^2 was demonstrated for a $\text{Cu/Cu}_2\text{O}$ cell. Analyses indicated that 10 to 11 mA/cm^2 is possible with current technology material. With improved material, values of 12 to 14 mA/cm^2 appear possible. There is much to be learned yet regarding effects of various impurities on the electronic properties of Cu_2O . However, only limited progress can be expected in this area during this contract period.

2. Cu₂O SUBSTRATE FABRICATION

2.1 Growth And Doping of Cu₂O

Studies of Cu₂O substrate fabrication have mainly involved efforts to develop controllably doped Cu₂O substrates. The current procedure for producing doped Cu₂O material is outlined in Figure 1. Copper discs are oxidized at 1050°C in a tube furnace while being supported by MgO. Crystalline MgO lumps (99.95% purity) are now used instead of less pure sintered material, and the dopant is introduced during the Cu₂O growth process. Previously, doped material was obtained by introducing the dopant after Cu₂O growth. Preliminary studies indicate that these two changes are providing improved material quality.

Doping occurs as a result of Cl vapor provided by MgCl₂. A source of MgCl₂ is typically held at a temperature between 200°C and 400°C. A continuous flow of Ar/O₂ transports the Cl vapor to the sample. Figure 2 gives results for resistivity versus MgCl₂ temperature. Each resistivity value refers to the average for a growth batch of six to eight samples.

The actual doping mechanism is not yet clear. However, measurements with an ion microprobe mass analyzer indicate that Cl is distributed fairly uniformly throughout Cu₂O grains. On the other hand, Mg was found to precipitate at grain boundaries. Two configurations which could lead to an acceptor level are: Cl enters the lattice as a neutral atom at an interstitial site; or substitutes for oxygen which results in a donor level, and also results in copper vacancy formation due to charge compensation effects.

2.2 Cu₂O Substrate Microstructure

Possible correlation of Cu₂O substrate microstructure with solar cell properties was investigated. These studies have involved fabrication of numerous small area devices on polycrystalline Cu₂O substrates. Figure 3 illustrates a key problem, namely, the variation of cell characteristics for devices on the same substrate. Although short-circuit current values are

GROWTH AND DOPING OF Cu_2O

Figure 1. Approach to Growth and Doping of Cu_2O .

Figure 2. Cu_2O Resistivity vs MgCl_2 Temperature.

NONUNIFORMITY IN SUBSTRATE PROPERTIES

Cu_2O SUBSTRATE WITH 19 CELLS
WITH 1.44mm DIAMETER. SUBSTRATE
DIAMETER = 1.5cm.

Figure 3. Picture of Cu_2O Substrate With Small Area Cells And
Typical I-V Curves.

Cu₂O MICROSTRUCTURE - SUBSTRATE SURFACE MORPHOLOGY

SMOOTH (110)

ROUGH (110)

ROUGH (111)

- POSSIBLE CORRELATION BETWEEN I-V. PARAMETERS AND SURFACE MORPHOLOGY HAVE BEEN EXAMINED. ALL CELLS WERE ETCHED WITH HBF.
- CELLS WITH PREDOMINANTLY SMOOTH GRAINS EXHIBIT BEST I-V CHARACTERISTICS.
- CELLS WITH PREDOMINANTLY ROUGH GRAINS EXHIBIT LOW VALUES OF R_{SH} AND LARGE VALUES FOR J_{01} (TUNNELING MECHANISM).

Figure 4. Optical Micrographs Cu₂O Substrate Surface Morphology.

Cu_2O MICROSTRUCTURE - CHANNELS

CHANNEL
CONNECTING
VOID REGION
TO SURFACE

VOID REGION
AT CENTER
PLANE

CROSS SECTION OF Cu_2O
SAMPLE AT 50X

ELEMENTAL DISTRIBUTION MAP
SHOWING CHLORINE IN CHANNEL

Figure 5. Optical Micrographs Showing Channels in Cu_2O .

always similar, diode current parameters vary considerably. More statistics are needed, but it appears that devices mainly containing "smooth" grains yield the best results. By smooth, or rough, we refer to the surface condition after being etched with HBF. Examples of "smooth" and "rough" surfaces are given in Figure 4.

Another feature of Cu_2O substrate microstructure which is being examined is that of channel formation. Figure 5 shows a cross-section of a sample of as-grown material which had a channel connecting the void region to the surface. Channels vary in size and may be responsible for low values of R_{SH} in some devices. Impurities may also concentrate in channels.

3. N-TYPE SEMICONDUCTOR FILMS

3.1 ZnS and ZnO

Further efforts were devoted to developing an approach to depositing conductive ZnS films by simultaneously depositing ZnS, Al, and Zn with a three source MBE system. However, problems were encountered in depositing Al from a Knudsen furnace. Discussions with other researchers indicate that a pyrolytic BN crucible may be needed. Purchase of a BN crucible is being considered.

We are particularly interested in the possible use of ZnO as a N-type partner to Cu₂O. An approach to depositing ZnO on Cu₂O must provide excess oxygen to avoid reduction of Cu₂O by free zinc. A fine leak valve was ordered for introduction of oxygen during deposition. While waiting for necessary parts to be used in ZnO deposition, discussions were held with Professor Don Brodie of the University of Waterloo concerning the possibility of having ZnO films deposited onto Cu₂O at his laboratory. Such a procedure was arranged. After preparing Cu₂O substrates, they were stored in a plastic bag with argon and sent to Brodie. One of the two substrates had a reasonably conductive and clear ZnO film on it. A diode did exist, but was very leaky and exhibited no photovoltaic behavior. Although, Professor Brodie has reported results in the past which indicate that high quality ZnO films were deposited, the films deposited on our Cu₂O samples appeared to be Zn-rich. As a result, this first attempt at a ZnO/Cu₂O heterojunction was not very productive.

3.2 Other Materials

Copper halides and Tl₂O₃ also appear to be candidate N-type materials for Cu₂O. Figure 6 summarizes the important parameters of candidate N-type materials. Tl₂O₃ is identified as interesting because thermodynamic considerations indicate that Tl should not reduce Cu₂O, and there are reports in the literature indicating that Tl₂O₃ is n-type and a wide bandgap semiconductor. Copper halides appear to be worthy of investigation because they are wide bandgap materials, readily formed on Cu₂O and CuF has a very good lattice match with Cu₂O.

N - TYPE SEMICONDUCTORS

Cu₂O PROPERTIES

- $X \approx 3.2$ eV
- $E_g = 1.9$ eV
- Crystal Structure:
Cubic
 $a_o = 4.27$ Å

DESIRABLE PROPERTIES FOR N-TYPE MATERIAL

- $E_g > 2$ eV
- $X < 4.8$ eV
- a_o OR $\sqrt{2} a_w$ 4.27 Å
- DESIRABLE THERMODYNAMIC PROPERTIES

MATERIAL	TYPE	E_g (eV)	X (eV)	a_o OR $\sqrt{2} a_w$ (MISMATCH)	POSSIBLE REACTION WITH Cu ₂ O
ZnO	N	3.3	4.0	4.63 Å (7.8%)	YES (#1)
ZnS	N	3.6	3.9	5.39 Å (21%)	YES (#1 & 2)
Tl ₂ O ₃	N	-	-	10.54 Å	NO (#3)
CuF	-	>3	-	4.26 Å (0.2%)	NO (#4)
CuBr	-	2.95	-	5.69 Å (25%)	NO (#5)

REACTION			$\Delta G(k \cdot Cal/g \cdot mole)$
(1)	$Zn + Cu_2O \rightarrow$	$2Cu + ZnO$	-41.0
(2)	$ZnS + Cu_2O \rightarrow$	$Cu_2S + ZnO$	-12.3
(3)	$(2/3)Tl + Cu_2O \rightarrow$	$(1/3)Tl_2O_3 + 2Cu$	+13.9
(4)	$F_2 + Cu_2O \rightarrow$	$2CuF + 1/2 O_2$	-47.5
(5)	$Br_2 + Cu_2O \rightarrow$	$2CuBr + 1/2 O_2$	-13.9

Figure 6. Summary of Pertinent Data For Candidate N-Type Partners In A Cu₂O Heterojunction.

Tl₂O₃ films were grown by oxidizing Tl films which had been deposited on quartz. The resistivity of these films approaches 10^{-3} Ω -cm after being exposed to oxygen. Optical transmission curves taken for these films indicate a band edge at approximately 400 to 450 nm (or, approximately 3eV). The results for electrical and optical properties of Tl₂O₃ films agree with reported results for sputtered films.

Preliminary experiments have been conducted regarding copper halide formation. Attempts to grow CuCl on Cu₂O involved reacting a Cu₂O substrate with vapor from CuCl₂ held at 300°C. A N-type film was formed on Cu₂O on several occasions with this procedure. At this time, it is not clear whether or not the films were CuCl or Cl-doped regions. Conditions have not been determined for which the films are stable under ambient conditions.

4. Cu₂O SOLAR CELL STUDIES

Cu₂O solar cell studies have concentrated on two areas, further study of current mechanisms in Cu/Cu₂O cells and investigation of Tl/Cu₂O Schottky barriers. Cu/Cu₂O devices are being studied in an effort to develop further understanding of current mechanisms in Cu₂O solar cells. Tl/Cu₂O device studies are motivated by the possibility of improved solar cell performance as a result of the large theoretical built-in voltage, and due to the predicated stability of a Tl-Cu₂O interface.

4.1 Cu/Cu₂O Device Studies

In previous reports, it was reported that two current mechanisms were indentified as contributing to I-V characteristics, one at low voltages (0 to 0.3 Volts) and one at larger voltages (>0.3 Volts). Detailed studies have been carried out to more fully understand Cu-Cu₂O cell characteristics. Results of these studies were reported previously. The low voltage mechanism was identified as a multiple step tunneling mechanism. The current is give by

$$J_1 = J_0 \exp(BV)$$

$$J_{01} = J_0 \exp(\epsilon/kT)$$

where V is the voltage across the load, and B is essentially temperature independent. The high voltage mechanism was identified as corresponding to thermionic emission of majority carriers over the metal-semiconductor barrier. Figure 7 summarizes theory pertinent to the two mechanisms.

Results of I-V analyses were further analyzed to determine if I-V parameters could be correlated with substrate micro-structure. Some results of this study are tabulated in Table 3. Parameters are given for two small area cells on two different substrates. In particular, 80FP14 and 80FP15 refer to two substrates, while the last number designates the small area cell on

THEORY FOR Cu-Cu₂O CELL CHARACTERISTICS

$$I = I_{o1} \exp(B_1 V_j) + I_{o2} \left[\exp\left(\frac{V_j}{n_2 kT}\right) - 1 \right] + \frac{V_j}{R_{SH}}$$

$$V_j = V - R_S I \quad (\text{DARK CHARACTERISTICS})$$

$$J_{o1} \sim \exp\left(-\frac{\epsilon}{kT}\right)$$

$$n_2 = 1 + \alpha$$

$$J_{o2} = A^* T^2 \exp\left[-\left(\chi \frac{1}{2} \delta + \frac{\phi_{BP}}{kT}\right)\right] \quad \chi_v \text{ in eV}, \quad \delta \text{ in } \text{\AA}$$

$$\phi_{BP} = \gamma \phi_{BO} + (1 - \gamma) \phi_o + \Delta\phi_{FC} \quad \text{eV}$$

$$\phi_{BO} = E_g + \chi - \phi_m$$

$$\gamma = (1 + \alpha)^{-1}$$

$$\alpha = (.181) \frac{D_s \delta}{K_i}$$

$$\Delta\phi_{FC} \approx \frac{N_{FC} \delta}{2K_i} \quad \text{eV}$$

$$D_s = \text{Density of Surface States } (10^{13} \text{ cm}^{-2})$$

$$K_i = \text{Relative Dielectric Constant of I-Layer}$$

$$N_{FC} = \text{Density of Fixed Positive Charge in I-Layer } (10^{15} \text{ cm}^{-2})$$

$$(\phi_B)_{PH} \approx \phi_{BP} + \chi_v$$

Figure 7. Summary Of Theory For I-V Characteristics of MIS Structure.

TABLE 3

I - V PARAMETERS FOR Cu - Cu₂O CELLS

CELL	80FP14-6	80FP14-15	80FP15-9	80FP15-15
SUBSTRATE RESISTIVITY (Ω -cm)	319	319	175	175
B ₁	12.9	9.09	6.78	6.03
J _{o1} (A/cm ²)	9.75×10^{-6}	8.25×10^{-4}	7.95×10^{-5}	1.15×10^{-4}
n ₂	1.13	1.15	1.09	1.08
J _{o2} (A/cm ²)	4.18×10^{-9}	8.67×10^{-9}	11.1×10^{-9}	9.36×10^{-9}
R _s (Ω)	130	99.3	90.6	91.0
R _{SH} (k Ω)	20.6	6.47	41.7	4.39
ROUGH SURFACE (%)	40	80	0	15
SMOOTH SURFACE (%)	60	20	100	85
GRAIN BOUNDARY LENGTH (mm)	11.4	9.8	20.3	11.6

- NOTES: 1. ROUGH SURFACES INCLUDE GRAINS WITH (111) AND (110) ORIENTATIONS, AND OTHER UNKNOWN ORIENTATIONS.
2. OBTAINED BY MEASURING GRAIN BOUNDARY LENGTH ON OPTICAL MICROGRAPH TAKEN AT 100X.

TABLE 4

BARRIER HEIGHT AND INTERFACIAL-LAYER PARAMETERS

CELL	ϕ_{BP} (eV)	$x_v^{1/2}\delta$	$(\phi_B)_{PHOTO}$ (eV)	x_v (eV)	δ (Å)
80FP14-6	.719	7.12	.930	.211	15.5
80FP14-15	.500	10.9	.960	.360	18.2
80FP15-9	.706	7.06	.940	.234	14.6
80FP15-15	.636	9.20	.920	.280	17.4

NOTES:

(i) ϕ_{BP} AND $x_v^{1/2}\delta$ DETERMINED FROM J_{O2} VS. T DATA, ASSUMING

$$J_{O2} = A \cdot T^2 \exp\left(-\frac{\phi_{BP}}{kT}\right) \exp(-x_v^{1/2}\delta)$$

(ii) $(\phi_B)_{PHOTO}$ DETERMINED FROM LONG WAVELENGTH PHOTORESPONSE.

(iii) x_v AND δ DETERMINED FROM VALUES FOR $(-x_v^{1/2}\delta)$ AND ASSUMING

$$(\phi_B)_{PHOTO} = \phi_{BP} + x_v$$

the particular substrate. The area of the cells is $.065 \text{ cm}^2$. Typically, a given cell includes several grains. The fraction of total area covered by smooth and rough surface is expressed as a percentage. In addition, the length of grain boundaries is given. It seems clear that no correlation can be made between R_{SH} and grain boundary length. On the other hand, the largest value of R_{SH} was exhibited by the cell which was essentially completely smooth. It should also be noted that the tunneling term J_0 is largest for the cell with a high percentage of area being rough. Further statistics are needed to make definite conclusions. Tentatively, we conclude that shunting paths and tunneling paths are distributed effects.

Interface parameters deduced for some Cu/Cu₂O cells are given in Table 4. The high voltage mechanism is best explained by a MIS model. The barrier heights are on the order of 0.5 to 0.7 eV, while the interfacial layer thickness is $\approx 14 \text{ \AA}$ to $18 \text{ \AA}$.

4.2 Tl/Cu₂O Device Studies

Thallium appears to be the only low work function metal that will not reduce Cu₂O. Since the work function is 3.7eV, a Tl/Cu₂O Schottky barrier has a very large theoretical efficiency. The theoretical value for J_0 is on the order of 10^{-18} A/cm^2 . If a high quality Tl-Cu₂O junction can be fabricated, it is highly probable that recombination current will be the dominant loss mechanism. One would still expect that an AM1 efficiency of 10% is possible, however.

The various factors which have motivated us to investigate Tl/Cu₂O cells are summarized in Figure 8. The change in free energy per mole of Tl is plotted versus temperature for Tl reacting with Cu₂O and CuO. The change in free energy for Tl reacting with Cu₂O is positive below 1300°K. Thus, it should be possible to deposit Tl onto Cu₂O without a reaction occurring.

The Tl/Cu₂O effort involves two aspects, fabrication and characterization of thick film Schottky barriers and development of an approach to depositing a conductive, thin film of Tl. The goal of the effort is to determine the junction parameters with thick film cells, and in a parallel effort determine procedures for depositing a thin conductive film of Tl.

TI/Cu₂O CELLS - BASIS FOR INVESTIGATION

THEORETICAL BARRIER HEIGHT

$$\Phi_{BP} = E_g + \Phi_m$$

$$\approx 1.5 \text{ eV}$$

$$J_0 \approx 10^{-18} \text{ A/cm}^2$$

$$V_{oc} \approx 0.96 \text{ V IF } J_{sc} = 10 \frac{\text{mA}}{\text{cm}^2}$$

$$\text{AM1 EFF} \approx 10.1\%$$

THERMODYNAMIC CONSIDERATIONS

AT RM TEMPERATURE

$$\Delta G = 2.4 \frac{\text{kCal}}{\text{Mole}}$$

$$\Delta G = 0.4 \frac{\text{kCal}}{\text{Mole}}$$

Figure 8. Electronic and Thermodynamic Considerations Which Indicate TI/Cu₂O Schottky Barriers Should Be Considered.

Tl films do not form a protective oxide surface layer. As a result, one can not simply deposit $100 \text{ \AA}$ of metal and quickly determine an approximate value for sheet resistance. It has been necessary to measure sheet resistance of thin films by determining resistance in situ as the film is grown. Figure 9 describes results obtained for Tl films deposited on a substrate held at room temperature. The sheet resistance depends on the deposition rate and film thickness. As indicated in Figure 9, the sheet resistance is essentially infinite until a thickness of $400 \text{ \AA}$, or more, is accumulated. Clearly, a thin metal Schottky barrier can only be made if films can be deposited with thicknesses on the order of $100 \text{ \AA}$ and with a sheet resistance in the range of $100 \Omega/\square$.

A key problem with deposition of Thallium is that the metal tends to agglomerate. Figure 10 shows an optical micrograph for a thick Tl film ($996 \text{ \AA}$ according to the monitor). The picture clearly shows that the film consists of alternately thick and thin regions. The effect of agglomeration is that a film mass equivalent to $400 \text{ \AA}$ of a film with a uniform thickness must be deposited before the film is connected--that is, such that electrical conduction can occur.

The agglomeration effect occurs as a result of lateral diffusion. As a result, agglomeration effects can be inhibited if the substrate is cooled. This approach will be used in an effort to deposit thin Tl films with adequate sheet conductance. Fixturing is being made which provide substrate cooling with cold nitrogen from a LN dewar.

Tl/Cu₂O cell fabrication has primarily involved thick Tl films. Preliminary results of I-V analyses indicate that two current mechanisms are still operative. However, the value of J_{02} appears to be on the order of 10^{-11} to 10^{-10} A/cm^2 at room temperature. Illuminated I-V characteristics have been monitored for some of the thick film devices as the Tl film slowly oxidizes in air. As the oxide region nearly consumes the complete Tl film, the transmitted light intensity is sufficiently high to give illuminated I-V characteristics. Figure 11 shows an example of such results. Note the large value of V_{OC} . These results are quite encouraging. It is clear that a significant built-in voltage is achieved at the junction of such a device.

TI/Cu₂O CELLS - THALLIUM FILMS ON RM TEMP SUBSTRATE

- SHEET RESISTANCE AND FILM THICKNESS RECORDED DURING DEPOSITION.
- FILMS DEPOSITED ON QUARTZ OR Cu₂O BECOME CONDUCTIVE AT ≈ 400 Å.
- OPTICAL MICROGRAPHS OF FILMS SHOW EFFECTS OF AGGLOMERATION

Figure 9. Sheet Resistance of Thallium Films Measured In Situ As Film Is Deposited.

TI/Cu₂O CELLS - THALLIUM FILM AGGLOMERATION

- TI FILM DEPOSITED ON QUARTZ AT ROOM TEMPERATURE.
- THICKNESS = 996 Å.
- MICROGRAPH SHOWS ISLANDS ON ORDER OF 1 μm IN DIAMETER.

(800 X)

Figure 10. Optical Micrograph of Thick Thallium Film Showing Effects of Agglomeration.

TI/Cu₂O SCHOTTKY BARRIERS

THEORETICAL PERFORMANCE

$$\Phi_m = 3.7 \text{ eV}$$

$$\Phi_{BP} = 1.5 \text{ eV}$$

$$J_0 = 8 \times 10^{-19} \text{ A/cm}^2$$

ASSUMING I-V DOMINATED
BY RECOMBINATION
CURRENT,

$$J_{OR} \sim 2 \times 10^{-17}, n = 2$$

AM1 EFF $\approx$ 9% TO 13%

CELL FABRICATION

- TI READILY OXIDIZED IN AIR.
- EVENTUALLY NEED PROTECTIVE LAYER.
- FIXTURING BEING MODIFIED FOR DEPOSITION OF PROTECTIVE AR.
- WORK TO DATE HAS INVOLVED THICK TI LAYERS.

CELL 80FP25A

TI / Cu₂O SCHOTTKY BARRIER

TI LAYER THICKNESS = 1000 Å

CELL AREA = 0.065 cm²

ILLUMINATION AM1

$$J_{sc} = 1.67 \text{ mA/cm}^2$$

$$V_{oc} = 0.65 \text{ VOLTS}$$

Figure 11. Illuminated I-V Characteristics of TI/Cu₂O Schottky Barriers.

5. FUTURE WORK

Efforts during the next six months will concentrate on the following:

- (i) Investigate copper halide formation on Cu_2O ;
- (ii) Investigate ZnO deposition onto Cu_2O ;
- (iii) Characterize $\text{Tl/Cu}_2\text{O}$ Schottky barriers in detail.

APPENDIX A
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