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INVESTIGATION OF SOLAR CELLS BASED ON Cu_2O
Final Progress Report for Period May 1, 1979—April 30, 1980

By
Larry C. Olsen

June 30, 1980

Work Performed Under Contract No. AC02-79ET23006

Dist-258
NTIS-22

Joint Center for Graduate Study
University of Washington
Richland, Washington

U.S. Department of Energy

Solar Energy

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05/01/79 - 04/30/80

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By

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ABSTRACT

This report discusses investigations conducted over a 12-month period concerning Cu_2O as a material for low-cost solar cells. Emphasis was placed on (i) Cu_2O substrate fabrication and characterization; (ii) studies of Cu_2O cell photocurrent; (iii) Cu_2O solar cell studies. Large grain polycrystalline Cu_2O substrates were fabricated by first oxidizing copper discs at 1050°C , and then polishing both sides to obtain 20 mil thick wafers. Optical constants were measured with ellipsometry and investigations of material microstructure were conducted. Photocurrent studies have included measurements of the internal photoresponse of $\text{Cu-Cu}_2\text{O}$ Schottky barriers, and computer aided analyses to optimize the structure of such cells in order to achieve maximum photocurrent. As a result, a photocurrent of 8.52 mA/cm^2 has been demonstrated with a $\text{SiO}(900 \text{ \AA})/\text{Cu}(90 \text{ \AA})/\text{Cu}_2\text{O}$ cell structure. Solar cell studies have concentrated on $\text{Cu-Cu}_2\text{O}$ MIS structures. Improved Cu_2O surface preparation procedures were developed. Depth concentration profiles taken with Auger spectroscopy indicate that the copper-to-oxygen atomic ratio is essentially two, after one or two monolayers are removed. An AM1 efficiency of 1.76% was obtained with a $\text{Cu-Cu}_2\text{O}$ cell. I-V analyses indicate that two current mechanisms are involved. A low voltage current component was identified as a thermally activated tunneling process, while a higher voltage mechanism is explained by an MIS model. The interfacial region is possibly a CuBr layer. The high voltage current component is characterized by $n \approx 1.15$ and $J_0 \approx 2 \times 10^{-9} \text{ A/cm}^2$. Efforts are underway to eliminate the tunneling component and improve cell I-V characteristics by optimizing the MIS structure.

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1. INTRODUCTION AND BACKGROUND MATERIAL

This report summarizes work done at the Joint Center for Graduate Study concerning Cu_2O solar cells. The program was funded by the Department of Energy as a result of a proposal written in response to PRDA ET-78-D-04-0039.

The overall objective of this program is to develop low-cost solar cells based on Cu_2O . Emphasis has been placed on fabrication and characterization of MIS and heterojunction cell structures which have potential efficiencies on the order of 10%.

The remainder of Section 1 contains brief discussions regarding the basis for Cu_2O as a photovoltaic material, a historical perspective, key technical issues, and key results obtained during this first year effort. Section 2 concerns growth of Cu_2O and characterization of the material. Investigations related to n-type semiconductor films are presented in Section 3, and photocurrent studies are described in Section 4. Cu_2O solar cell studies are discussed in Section 5, and future work is considered in Section 6.

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 junction formed either by a homojunction, or a heterojunction. The maximum photocurrent that can be generated by a cell based on Cu_2O

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

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 by¹

$$J_{01} \approx 10^8 \times (e^{-E_g/kT}) \frac{A}{\text{cm}^2}$$

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 of¹

$$J_{0r} \approx e^{-E_g/2kT}$$

For Cu₂O, J_{0r} ≈ 2 x 10⁻¹⁷ A/cm² and the corresponding maximum efficiency is 13%.

Investigations of Cu₂O solar cells made to date suggest that a photo-current 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 Cu_2O 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 Cu_2O 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 Cu_2O , this step may ultimately be very simple. Copper sheet can be oxidized at 1000°C to obtain large grain polycrystalline material. For example, 5-mil copper sheet can be allowed to oxidize at 1000°C to achieve Cu_2O sheet with grains several millimeters wide. Copper sheet can also be partially oxidized to obtain Cu_2O films with grain sizes several hundred μm wide. A partially oxidized copper substrate results in a

Cu_2O -Cu junction, however. This interface is the basis of the so-called Cu/Cu₂O backwall rectifier. If a Cu₂O film grown in this manner is to be utilized for efficient, thin-film solar cell structures, the copper would have to be removed and replaced by an ohmic contact or fabrication procedures developed such that the backwall junction is essentially an ohmic contact.

One other point should be made regarding the motivation for photovoltaic investigations of Cu₂O. Since the band gap is approximately 2.0 eV, Cu₂O is candidate material for one cell of a two-cell system. In addition, Cu₂O may also be very compatible with a low-cost luminescent concentration system.

1.2 Historical Perspective

The first device based on Cu₂O was a backwall copper-oxide rectifier. This device was fabricated by L. Grondahl in 1920. During the 1920's and early 1930's, development efforts were carried out to correlate rectifier characteristics with fabrication techniques. Grondahl summarized these efforts in 1933.² Grondahl also reported preliminary results on a front-wall photocell made by reducing the surface of Cu₂O to form a Cu/Cu₂O Schottky barrier. He reported a photoresponse of ~50% at 500 nm. No effort was made to characterize the device as a solar cell. Only the measured photoresponse at 500 nm was mentioned.

In the 1940's, efforts were carried out at Bell Labs by Bardeen, Brattain, and Shockley to develop a basic understanding of the copper oxide rectifier. During this time period, models for Schottky barriers were developed. Interest also began to be transferred to silicon. Again, no effort was made to develop Cu₂O solar cells. Brattain published a review of this work in 1951.³

Assimos and Trivich published results concerning the photoresponse of frontwall Cu/Cu₂O cells in 1973.⁴ In 1975, two programs specifically aimed at Cu₂O solar cell fabrication and characterization were initiated by NSF RANN, one at Wayne State and one at JCGS. Both programs were relatively small. Both groups investigated frontwall Schottky barrier cells. Power conversion efficiencies approached 1% by 1978. Due to increased funding, the JCGS group has made significant progress during the current effort.

The Cu_2O solar cell efficiency has been increased to 1.76%.

It should be strongly emphasized that the total integrated effort devoted to Cu_2O solar cell research and development is insignificant, compared to other materials presently being investigated. The rather crude investigations conducted on backwall rectifiers in the 1920's and 1930's are often mistakenly regarded as work related to solar cell development. Semiconductor physics had not yet been developed. In fact, Brattain's work published in 1951 concerns strictly backwall cells fabricated by partially oxidizing copper substrates. These devices are not of interest to solar cell studies.

1.3 Key Technical Issues

There are three key technical issues concerning the ultimate viability of Cu_2O as a photovoltaic material, namely:

- (i) Photocurrent
- (ii) Junction formation
- (iii) Current-mechanisms

In order to develop Cu_2O solar cells with efficiencies in the 8 to 10% range, cell photocurrents must eventually approach 12 mA/cm^2 . A value of 8.52 mA/cm^2 has been demonstrated with a $\text{Cu/Cu}_2\text{O}$ device. Analytical studies indicate that achievement of 10.5 mA/cm^2 is possible with a heterojunction structure, if the internal photoresponse of such a cell is the same as that measured for $\text{Cu/Cu}_2\text{O}$ frontwall cells. The final step taken to obtain 12 mA/cm^2 will probably involve increasing the internal photoresponse by improving the minority carrier diffusion length, and/or development of approaches to enhance dissociation of excitons in the low wavelength range.

Since no approach to doping Cu_2O n-type is known, we must consider a heterojunction, MIS cell, or Schottky barrier for a device structure. Studies of Schottky barriers have shown that most metals reduce Cu_2O to form a copper-rich layer adjacent to Cu_2O . As a result, the Schottky barrier cells studies exhibited properties essentially like $\text{Cu/Cu}_2\text{O}$ devices. It appears, therefore, that either a heterojunction or MIS cell structure must be developed. Encouraging results have been obtained with both types of devices.

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. Progress made during the past year related to identification of current mechanisms in Cu₂O cells, suggests that there is no basic reason to prevent the required reduction in J_0 .

1.4 Key Results of This Program

Very significant results have been achieved during the current effort. A Cu₂O cell was fabricated with an efficiency of 1.76%, and a short-circuit current of 8.52 mA/cm² was achieved. Key results obtained to date are summarized in Table 3.

Table 3
KEY RESULTS OF THIS PROGRAM

MATERIAL CHARACTERIZATION

- Optical absorption coefficient measured with ellipsometry.
- Established Cu₂O growth procedure with relatively narrow resistivity range

PHOTOCURRENT STUDIES

- Internal photoresponse measured for Cu₂O cells.
- Frontwall Cu/Cu₂O cell structure optimized to maximize photocurrent.
- Demonstrated photocurrent:

$$J_{PH} = 8.52 \text{ mA/cm}^2$$

SOLAR CELL STUDIES

- MIS structure tentatively identified as Cu/(CuBr)/Cu₂O pursued. Demonstrated active-area efficiency:
AM1 Efficiency = 1.76%
- Dark I-V characteristics of Cu/(CuBr)/Cu₂O cells analyzed. Two current components identified. One component typically is described by

$$J_0 = 2 \times 10^{-9} \text{ A/cm}^2$$

$$n = 1.15$$
- MIS cells based on SiO₂ I-layer explored. Enhanced voltages obtained. Key problems identified.
- Investigations of n-type ZnS and ZnO films initiated.
- ZnO/Cu₂O heterojunction fabricated with $V_{OC} = 0.42$ V.

2. Cu₂O PREPARATION AND CHARACTERIZATION

2.1 Preparation of Cu₂O Substrates

During this past year, emphasis has been placed on cell fabrication based upon large-grain polycrystalline Cu₂O substrates. These substrates are grown by completely oxidizing a copper wafer in O₂ atmosphere. Typically, eight to ten copper discs 3/4 inches in diameter and 50 mils thick are oxidized in a given run. The discs are placed on a bed of MgO lumps which are uniformly distributed across a quartz boat. The discs are oxidized in a tube furnace at 1050°C with a mixture of oxygen and argon gas flowing. Cu₂O reacts to some degree with MgO, but in a tolerable manner.

Since the oxidation of copper occurs by vacancy diffusion, the oxidized copper wafer has voids at the center plane as indicated in Figure 1. Cu₂O substrates are prepared by grinding on one side of the as-grown sample until past the void region. The other sample face is then sanded and polished. The last polishing step is done with 0.25 μm diamond paste. The highly polished face is utilized for junction formation. An ohmic contact is eventually applied to the unpolished face.

The resistivity of Cu₂O substrates grown by using 99.95% pure with no intentionally added dopant exhibit resistivities on the order of 1000 Ω-cm. Procedures have been developed for controllable doping Cu₂O and obtaining resistivities in the range of 50 Ω-cm to 500 Ω-cm.

2.2 Doping Studies

During the first three quarters of this program, Cu₂O substrates were grown using MgO lumps obtained by breaking MgO combustion boats. This material is much more porous than the MgO material now used. During that period, substrates were used both in the as-grown condition and after subjecting them to an additional doping step.

During the fourth quarter of this program, a refined procedure for doping Cu₂O substrates was developed. Cu₂O samples were subjected to vapor from a MgCl₂ source during the copper-oxidation step. Precautions are taken to insure that the MgCl₂ source is free of H₂O. The dopant source is

Figure 1. Cross-Section of As-Grown Cu_2O Sample.

held at a temperature in the range of 100°C to 400°C. The mechanism for doping is not yet clear. A yellow residue left on the quartz tube has been analyzed to be CuCl_2 , while residue remaining in the dopant crucible has been identified as MgO . Elemental analyses obtained on material doped by a similar method indicated that both Mg and Cl enter the Cu_2O material. Both Cl and Mg would be expected to act as a donor if substituted into the Cu_2O lattice, since Cl would most likely enter an oxygen site and Mg enter a Cu site. However, the doping procedure results in increased p-type conductivity. A possible explanation of these results is that Mg and Cl enter the Cu_2O lattice as suggested, but that a copper vacancy is formed for each added impurity. Copper vacancies are known to act as acceptors.

The current procedure used for doping has produced consistent results concerning resistivity. Results for substrate resistivity and dopant-source temperature are tabulated in Table 4.

2.3 Optical Constants of Cu_2O

Efforts were devoted to determining optical constants for Cu_2O this year. Ellipsometric measurements were made on polycrystalline substrates identical to those used for solar cell fabrication. Narrow band pass filters were used in conjunction with the ellipsometer light source to obtain measurements at various wavelengths. Results could not be obtained for wavelengths near the band edge due to large limits-of-error associated with the measurement.

Values for optical absorption coefficient for Cu_2O are shown in Figure 2. Values determined in this work are given along with results reported in the literature. Studies reported by Baumeister were carried out on samples similar to those used in this program. The results of Brahms and Nikitine were obtained for oxidized films of copper on quartz. The dashed line in Figure 2 indicates values of α vs λ that are assumed for Cu_2O in photoresponse analysis. Values of α , as well as the real and imaginary parts of the index of refraction, are tabulated in Table 5.

Table 4
PROPERTIES OF Cu_2O SUBSTRATES DOPED WITH MgCl_2 SOURCE

GROWTH RUN	NUMBER OF SAMPLES	MgCl_2 TEMPERATURE ($^{\circ}\text{C}$)	AVERAGE RESISTIVITY ($\Omega\text{-cm}$)
800613	4	no dopant	1175
800516	4	100	398
800509	6	150	375
800502	3	200	216
800523	4	200	269
800424	5	280	262
800417	4	450	85

Table 5
OPTICAL CONSTANTS USED FOR Cu_2O CALCULATIONS

λ (nm)	N	K	α^{-1} (cm^{-1})
350	3.4	0.96	3.05×10^5
375	3.4	0.96	3.05×10^5
400	3.4	0.96	3.05×10^5
425	3.4	0.91	2.7×10^5
450	3.4	0.78	2.2×10^5
475	3.4	0.30	8.0×10^4
500	3.4	.040	1.0×10^4
525	3.25	.026	6.2×10^3
550	3.1	.0175	3.9×10^3
575	3.0	.0087	1.9×10^3
600	2.9	.0033	690
625	2.8	7.0×10^{-4}	140

Figure 2. Cu_2O Optical Absorption Coefficient.

3. N-TYPE SEMICONDUCTOR FILMS

One objective of this program was to investigate ZnO and ZnS as possible n-type films to be utilized on a heterojunction with Cu_2O . Approaches to depositing these films consisted of reactively sputtering ZnO and vacuum depositing ZnS. Both a sputtering system and an appropriate evaporator for ZnS had to be constructed. A sputtering system was assembled in the first quarter and investigations of ZnO films initiated. A three-source evaporator system referred to as an MBE system, was completed early in the fourth quarter.

3.1 Reactively Sputtered ZnO Films

Reactively sputtered ZnO films were deposited with good optical properties and reasonable electrical properties. Sputtering parameters and film properties for typical ZnO films are given in Table 6. As indicated, the films are occasionally conductive as deposited. Indium doping was achieved by placing pieces of In on the Zn target. The percentage refers to the percentage of target area covered by In. Optical transmission curves for two films deposited on quartz are given in Figure 3. Both films were conductive.

The approach utilized to obtain results described by Figure 3 and Table 6 involved establishing a d.c. discharge between a planar electrode and a disc shaped target. After obtaining these results, attempts were made to fabricate devices. Although enhanced V_{oc} values were obtained in some cases, cells were generally of rather poor quality. As a result, it was decided to build new fixturing which would include a shutter in front of the sample holder. A cylindrical geometry was chosen; in particular, a zinc rod is utilized as the negative electrode and a concentric aluminum cylinder is used as the positive electrode. A sample carrousel is rotated over an axially oriented rectangular opening in the aluminum cylinder. Zinc oxide is reactively sputtered with a d.c. discharge. The arrangement allows one to establish and maintain a discharge for any desired length of time prior to exposing of samples to sputtered material since the cylindrical arrangement effectively contains the discharge. Water cooling of the zinc rod was accomplished by drilling a hole in the zinc rod and inserting an aluminum tube to carry water.

Table 6.
SPUTTERED ZnO FILMS ON QUARTZ

Sample	Voltage and Current (mA)	Inlet Composition (Atmos.)	Pressure (μ m)	Time (min)	Dopant	Heat Treatment	Sheet Resistance ($\Omega/\square$)
5-16-79	1 kV 240 mA	11% O ₂ /89% Ar	30 μ m	21	--	--	4.06 x 10 ⁵ (As deposited)
5-20-79	1 kV 240 mA	20% O ₂ /80% N ₂	35 μ m	45	3% In	15 min at 500°C	1.45 x 10 ³
5-30-79	1 kV 240 mA	2.5% O ₂ /97.5% Ar	35 μ m	40	5% In	15 min at 500°C	4.04 x 10 ⁴
6-8-79	1 kV 240 mA	5% O ₂ /95% Ar	40 μ m	50	5% In	--	2.8 x 10 ⁵
6-20-79	1 kV 240 mA	100% O ₂	35 μ m	340	5% In	20 min in N ₂ - H ₂ at 500°C	1.1 x 10 ⁵
6-26-79	1 kV 250 mA	100% O ₂	30 μ m	60	--	5 min in N ₂ - H ₂ at 500°C	1.8 x 10 ⁴

N-TYPE FILMS - OPTICAL TRANSMISSION OF REACTIVELY SPUTTERED ZnO FILMS

FILM	5-20-79	6-20-79
INLET COMPOSITION	20% O ₂ / 80% N ₂	100% O ₂
HEAT TREATMENT	15 min @ 500°C	20 min @ 500°C In N ₂ -H ₂
SHEET RESISTANCE (Ω/□)	1.45×10^3	1.1×10^5

Figure 3. Optical Transmission of Reactively Sputtered ZnO Films.

3.2 ZnS Films

A three-source MBE system was constructed for deposition of ZnS films. An existing ion-pumped single-source evaporation system was modified to become a three-source MBE system. This system was finished and placed in operation in the fourth quarter. Three Knudsen cell furnaces coupled to a thermal controller are clustered at the bottom of the chamber. Shutters over the three sources are designed such that a single source can be utilized, or all three sources used simultaneously. This arrangement allows one to determine individual component deposition rates before actual film deposition. The substrate carrousel rotates and has eight positions for samples. A thickness transducer rests at the center of the carrousel. Quartz radiant heaters allow system bakeout up to 400°C. Shutters covering the samples also exist.

ZnS films deposited using the MBE system exhibit very good optical properties. Deposition of conductive films by co-depositing ZnS and In was attempted. These films were not conductive as deposited. One In-doped film became conductive after heat treatment at 600°C for one hour. The film was 4000 Å thick and exhibited a sheet resistance of $1.36 \times 10^6 \Omega/\square$. The optical transmission curve determined for this film is shown in Figure 4.

Previous studies using a less sophisticated deposition system resulted in as-deposited conductive films when Al was used as a dopant. Attempts to utilize aluminum in the present three-source system have not been successful. Al tends to plug the small opening in the Knudsen furnace. Discussions with other researchers indicate that better results are obtained with a pyrolytic boron-nitride inner crucible and a large opening. Such crucibles are on order for future studies. Prospects for obtaining as-deposited, conductive ZnS films appear promising, if a three-source deposition (ZnS, Al, Zn) is utilized.

3.3 Other Possible N-Type Films

During this past year, the thermodynamic stability of possible Schottky barrier, MIS, and heterojunction devices based on Cu_2O has been studied. One metal has been identified which should not reduce Cu_2O , namely, Tl. Free energy changes associated with the metal being in contact with Cu_2O are given

N-TYPE FILMS - OPTICAL TRANSMISSION OF ZnS FILMS ON QUARTZ

- FILM GROWN BY CODEPOSITION OF ZnS AND In.
ZnS @ 120 Å/min
In @ 7-10 Å/min
- GOOD OPTICAL QUALITY ACHIEVED AS DEPOSITED.
- FILM THICKNESS = 4000 Å
- SHEET RESISTANCE = $1.36 \times 10^6 \Omega/\square$
AFTER 1 HOUR @ 600°C
- FUTURE EFFORTS WILL INVOLVE CODEPOSITION OF ZnS, In AND Zn

Figure 4. Optical Transmission of ZnS Films on Quartz.

in Table 7. The work function of Tl is 3.7 eV. Thus, the use of Tl in a Schottky barrier structure appears attractive. Preliminary experiments indicate that thin films of Tl readily oxidize upon exposure to air.

Possible n-type films are also suggested by these thermodynamic considerations. Tl_2O_3 can also be formed on Cu_2O without reducing Cu_2O . Tl_2O_3 doped with Sn could possibly yield n-type films. Such films would represent an analog of ITO, that is $In_2O_3(SnO_2)$ films. The interesting and exciting possibility presented by these considerations is that a heat treatment step may not be detrimental to the cell physical structure.

Another possible heterojunction structure has been examined with respect to thermodynamic stability, namely, a possible structure involving a copper halide film on Cu_2O . Copper halide films can be readily formed on Cu_2O by reacting with the halogen. Free energy changes are given in Table 7. Studies of halide film formation are currently under way. Preliminary results indicate that a cupric oxide region forms between the copper halide and Cu_2O , if a reaction involving Cu_2O and the halogen is utilized. To form a $CuBr/Cu_2O$ junction, say, it may be necessary to provide copper vapor along with the bromine, or to react Br with a copper film previously deposited on Cu_2O .

Table 7
FREE ENERGY CHANGES

REACTION	$\Delta G(kCal/g-mole)$
1. $Cu_2O + 2 Tl \longrightarrow Tl_2O + 2 Cu$	+4.8
2. $Cu_2O + 2/3 Tl \longrightarrow 1/3 Tl_2O_3 + 2 Cu$	+13.9
3. $Cu_2O + F_2 \longrightarrow 2 CuF + \frac{1}{2} O_2$	-47.5
4. $Cu_2O + Cl_2 \longrightarrow 2 CuCl + \frac{1}{2} O_2$	-21.9
5. $Cu_2O + Br \longrightarrow 2 CuBr + \frac{1}{2} O_2$	-13.9

4. PHOTOCURRENT STUDIES

Detailed studies of Cu_2O cell photocurrent have been conducted to increase J_{PH} as closely as possible to the maximum value of 17.2 mA/cm^2 . Considerations of properties of copper films, carrier and photon losses, calculated values of photocurrent and experimental results for J_{PH} are discussed in the following subsections.

4.1 Properties of Copper Films

Electrical and optical properties of copper films have been investigated in order to optimize the $\text{Cu-Cu}_2\text{O}$ cell structure for maximum photocurrent. Sheet resistance and optical constants of copper films were measured as a function of film thickness. In order to maximize the efficiency of a $\text{Cu-Cu}_2\text{O}$ MIS cell, photon transmission through a copper film must be maximized, while the film sheet resistance must be maintained at an adequately low value.

Figure 5 gives a plot of sheet resistance versus film thickness for copper films deposited at a wide range of deposition rates. These films were deposited on quartz discs which had bar-shaped contacts separated by 1 cm. Resistance of the films between the two contacts was monitored during deposition. The results showed the effects of deposition rate, as well as thickness. If one uses a film thickness of $60 \text{ \AA}$ to $100 \text{ \AA}$, sheet resistances below $30 \Omega/\square$ can be achieved regardless of deposition rate. Films deposited at rates in excess of $20 \text{ \AA/sec.}$ exhibit lower resistivities for films on the order of $90 \text{ \AA}$. Slowly deposited films clearly nucleate in a more homogeneous manner, since such films exhibit finite conductance at lower values of film thickness. Films deposited at very fast rates apparently agglomerate in islands which do not join until the thickness monitor reads $30 \text{ \AA}$ to $40 \text{ \AA}$.

$\text{Cu-Cu}_2\text{O}$ cell studies have utilized films deposited at rates on the order of 10 to $15 \text{ \AA/sec.}$, and which are approximately $90 \text{ \AA}$ thick. This choice of film thickness resulted in maximum photocurrent for the chosen range of deposition rate. Further studies should be conducted concerning slowly deposited films, however.

Figure 5. In Situ Measurement of Sheet Resistance for Vacuum Deposited Copper Films.

Figure 6 gives optical constants for films deposited at rates between 10 and 15 Å/sec. N and K are the real and imaginary parts of the index of refraction. Note that minimum values of K occur for films in the 80 Å to 90 Å thickness range. These results were obtained by measuring transmission and reflection versus wavelength for films deposited on quartz.

Calculated values for photon transmittance into Cu_2O for $\text{Cu-Cu}_2\text{O}$ cells with SiO_2 antireflection coatings and copper films deposited at 10 to 15 Å/sec. are given in Figure 7. Maximum transmittance is obtained for films in the 90 Å range. These calculations were conducted using computer codes based on thin film optics analysis.

4.2 Internal Photoresponse for $\text{Cu/Cu}_2\text{O}$ Cells

Figure 8 gives plots of the internal photoresponse (S_λ) for four devices. S_λ is defined by $Q_\lambda = T_\lambda S_\lambda$, where Q_λ is the total photoresponse and T_λ is the photon transmittance into Cu_2O . Two of the cells were fabricated on very lightly doped material, and two on more heavily doped substrates. Detailed studies are now underway to characterize the photoresponse of cells fabricated with material doped during growth. There are interesting differences in S_λ at both the low wavelength and high wavelength ends of the range of λ where $S_\lambda > 0$.

Consider the low wavelength range of the photoresponse curve. Note the difference between the cells based on substrates lightly doped (as-grown) and more heavily doped (doped). S_λ is larger for the low resistivity material. Furthermore, note that S_λ for 78FP35 is midway between 79FP25 and 79FP27, even though substrates 35 and 27 have similar values of resistivity. The low wavelength effects are most likely associated with exciton dissociation. A significant fraction of photon absorption in Cu_2O is due to exciton absorption. An exciton must dissociate into a normal electron-hole pair before any photocurrent results. Probability of dissociation is enhanced in the vicinity of certain types of defects. Further study of these effects may eventually allow one to fabricate a cell with S_λ being large at both ends of the wavelength range.

Four exciton bands have been identified for Cu_2O , a yellow band

Figure 6. Optical Constants of Copper Films vs. Wavelength.

Figure 7. Photon Transmittance into Cu_2O .

INTERNAL PHOTORESPONSE

- INTERNAL PHOTORESPONSE (S_λ) DEFINED BY

$$Q_\lambda = T_\lambda S_\lambda$$

APPROACH

- SIMULTANEOUSLY DEPOSIT Cu ON Cu_2O AND QUARTZ
- UTILIZE Cu/QUARTZ SAMPLE TO DETERMINE n AND k OF Cu FILM
- CALCULATE T_λ AND R_λ FOR Cu/ Cu_2O CELL
- USE T_λ FOR Q_λ ANALYSIS AND COMPARE CALCULATED AND MEASURED R_λ

Figure 8. Internal Photoresponse for Cu/ Cu_2O Solar Cells.

(520 nm to 650 nm), a green band (480 nm to 540 nm), a blue band (450 nm to 490 nm), and a violet band (350 nm to 500 nm). The lower wavelength blue and violet bands are very sensitive to material processing. For example, Spyridelis found that an increase in copper vacancy concentration enhances photoconductivity.⁵ Photoresponse results shown for cells 79FP24 and 79FP27 are consistent with Spyridelis' measurements, since the lower resistivity material probably has a larger copper vacancy density. Aspects of material growth and/or substrate surface preparation appear to also affect S_λ at the low wavelengths. Cells 79FP35 and 79FP27 have similar resistivities, but yet, have significantly different values of S_λ in the short wavelength range.

The results for S_λ for photons with 500 nm to 650 nm are also very interesting. First, note that the effective band edge for Cu_2O corresponds to $\lambda \approx 650$ nm, of $h\nu \approx 1.91$ eV. The yellow exciton band is clearly playing a role in determining the photoresponse in this region. The electron band gap corresponding to normal band-to-band excitation is at ≈ 2.1 eV, or $\lambda = 590$ nm. The effect of exciton creation and subsequent dissociation into useful electron-hole pairs gives rise to effective edge of 1.91 eV (650 nm). A complete analysis of S_λ should probably involve exciton transport and recombination effects, as well as the usual considerations concerning minority carrier transport. However, it appears that the long wavelength region photoresponse can be explained by assuming photon absorption results in one electron-hole pair, whether by a normal band-to-band excitation, or via exciton creation and subsequent dissociation into a normal electron-hole pair. The internal photoresponse is then interpreted strictly in terms of minority carrier transport. Thus, we set S_λ to

$$S_\lambda = (1 - e^{-\alpha w}) + e^{-\alpha w} \left(\frac{\alpha L}{1 + \alpha L} \right)$$

Photoresponse data between $\lambda = 600$ nm and 650 nm has been interpreted using the above model for cells 78FP35 and 79FP24. Depletion widths were obtained using C-V data taken at 500 kHz. Minority carrier diffusion lengths were determined to be 12.3 μm for 78FP35, and 2.0 μm for 79FP24. These results suggest that with further improvement in material quality, significantly larger diffusion lengths can be obtained.

4.3 Calculated Photocurrent For Cu/Cu₂O Cells

Analysis of photocurrent from Cu/Cu₂O cells has been done in detail. Values of J_{PH} were calculated assuming a 90 Å copper film, and by varying the AR index of refraction. For a given AR index of refraction, the optimum AR film thickness was determined which maximized J_{PH} . Figure 9 gives J_{PH} vs. AR index of refraction. A value of 1.9 appears to be the best choice for a single AR coating, yielding 8.6 mA/cm². An index of refraction of 1.9 can be achieved for an SiO coating if the material is deposited rapidly and at pressures below 10⁻⁵ torr.⁶ SiO coatings obtained to date have been accomplished by depositing from an SiO source at a rate of 2 Å/sec., and at a pressure of $\approx 10^{-6}$ torr. Ellipsometric measurements indicate the index of refraction is typically 1.6. This value is consistent with results reported in the literature. Thus, by depositing SiO layers with an index of refraction near 1.9, J_{PH} of Cu/Cu₂O cells can be increased to 8.6 mA/cm².

4.4 Experimental Results

Significant progress has been made concerning photocurrent. Table 8 gives results for several cells. The devices are listed in the order they were fabricated. The value of J_{PH} has increased continually during this program. The increase is a result of continued improvement in device quality and the optimization procedures utilized. As indicated, a value of 8.5 mA/cm² has been demonstrated.

4.5 Photon and Carrier Loss Analysis

Since the internal photoresponse has been measured for Cu-Cu₂O cells, and optical constants have been determined for copper films, it is possible to carry out a detailed photon and carrier loss analysis for these devices. Figure 10 indicates where photons and carrier losses occur in a SiO(550 Å)/Cu(90 Å)/Cu₂O cell structure. Assuming an AM1 spectrum as observed for Phoenix, Arizona, the maximum possible photocurrent for Cu₂O is 17.2 mA/cm². First, consider the loss of photons by reflection and as a result of photon absorption in the copper film.

As indicated in Figure 10, 2.3% of the photons are reflected. The

PHOTOCURRENT - OPTIMUM AR COATING FOR Cu-Cu₂O CELLS

Figure 9 Photocurrent For Cu/Cu₂O vs. AR Coating Index Of Refraction.

Table 8
EXPERIMENTAL RESULTS FOR Cu_2O CELL PHOTOCURRENT BASED ON ACTIVE AREA

CELL NO. 79FP---	SUBSTRATE RESISTIVITY ($\Omega\text{-cm}$)	SiO_2 AR THICKNESS ($\text{\AA}$)	J_{SC} (mA/cm^2)	J_{PH}^* (mA/cm^2)	ACTIVE AREA (cm^2)
24	76	720	6.48	6.55	0.71
25	66	720	6.28	6.34	0.71
26	35	682	6.90	6.98	0.71
27	305	682	7.11	7.51	0.71
49-5	564	705	7.00	7.32	.060
55-11	465	700	7.83	8.00	.060
57-9	574	720	7.64	7.92	.060
58-13	352	702	8.33	8.52	.060

* Determined from

$$J_{\text{PH}} = J @ V = -R_s I$$

PHOTOCURRENT -- PHOTON AND CARRIER LOSS ANALYSIS

Figure 10. Photon and Carrier Loss Analysis for Cu/Cu₂O Solar Cells.

corresponding lost photocurrent is 0.4 mA/cm^2 . The photon flux lost due to absorption in the copper film is much larger, namely, 15.4% of the incident flux. The corresponding lost current is 2.65 mA/cm^2 . The total lost photocurrent due to reflected photons, and as a result of absorbed photons in the front layers, is approximately 3.0 mA/cm^2 .

The total photon flux transmitted into Cu_2O is approximately 82.3% of the incident photon flux. Assuming that each photon creates one electron-hole pair, the remaining possible photocurrent is 14 mA/cm^2 . Carrier losses occur primarily at the low wavelength region, and near the band edge (long wavelengths). Assuming S_λ vs. λ is given by the plot for cell 78FP35 in Figure 8, and utilizing calculated values for T_λ , one calculates that uncollected electron-hole pairs created by photons with $500 \text{ nm} \leq \lambda \leq 650 \text{ nm}$ constitutes a photocurrent increment of 3.57 mA/cm^2 , or 20.8% of the maximum possible photocurrent. Uncollected electron-hole pairs created by photons with $\lambda \leq 500 \text{ nm}$ is equivalent to a photocurrent increment of 1.98 mA/cm^2 , or 11.5% of the maximum photocurrent.

As indicated by Figure 10, the predicted J_{PH} is 8.60 mA/cm^2 . Carrier and photon losses are equivalent to 5.55 mA/cm^2 and 3.05 mA/cm^2 , respectively. Now, consider possible improvements in J_{PH} . Further optimization of the front layers (AR and metal film) may provide for an increase of 1 mA/cm^2 . This improvement would primarily come from reduction of absorption within the copper film. Further improvement in material quality should lead to longer minority carrier diffusion lengths, which may provide for an incremental improvement in J_{PH} of 2 mA/cm^2 . Improved understanding of the photoresponse at lower wavelengths should suggest an approach to obtain an additional 1 mA/cm^2 for J_{PH} . With these various improvements, J_{PH} would approach 12.5 mA/cm^2 .

Based on this detailed photon/carrier loss analysis, we project that J_{PH} for Cu_2O solar cells will eventually be in the 12 to 13 mA/cm^2 range.

5. SOLAR CELL INVESTIGATIONS

Solar cell structures investigated have included Schottky barriers, MIS, and heterojunction structures. Previous investigation of Schottky barrier devices led to the conclusion that all metals investigated reduced Cu_2O when deposited onto a substrate, thereby effectively forming a $\text{Cu}/\text{Cu}_2\text{O}$ cell.⁷ Since arriving at that conclusion, the JCGS program has concentrated on MIS and heterojunction structures. Solar cell studies have been supported by thermodynamic calculations, continued refinement of the approach to solar simulation and Cu_2O surface analysis. In this report, discussions are given concerning the AM1 simulation currently being used, recent results of Cu_2O surface analysis and performance of $\text{Cu}-\text{Cu}_2\text{O}$ MIS cells.

5.1 AM1 Solar Simulation for Cu_2O

Simulators based on ELH lamps are used by many groups for various types of cells. The irradiance spectrum characteristic of an ELH bulb is significantly different than a solar spectrum at low wavelengths. As a result, a simulator based on bare ELH lamps is inadequate for high band gap cells. An adequate AM1 simulation of Cu_2O can be obtained by filtering the light from ELH lamps. This simulator was further refined this past year. Irradiance data for the JCGS Cu_2O simulator are given in Figure 11.

5.2 Cu_2O Substrate Surface Preparation and Analysis

Very significant progress has been made concerning Cu_2O surface preparation prior to cell fabrication. After the final polishing step involving $0.25\text{ }\mu\text{m}$ diamond paste, cleaning and etching procedures are utilized as indicated in Table 9. The cleaning steps appear to be quite adequate. The HBF etching step provides a relatively flat surface. A very key step that has been taken is the last one involving a bromine-methanol etch. The bromine combines with excess copper and a very high quality surface results.

Figure 12 is a depth-concentration profile taken of a Cu_2O surface. The estimated sputtering rate is $15\text{ }\text{\AA}/\text{min}$. Note that after a depth of essentially one monolayer, the copper-to-oxygen ratio is ≈ 2 , and is constant. Figure 13 gives results for copper-to-oxygen ratio versus sputtering time for two Cu_2O samples. Sample 1 is the sample for which the

SOLAR CELLS - AM1 SOLAR SIMULATION

Figure 11 Approach to AM1 Simulation For Cu_2O .

Figure 12. Depth Concentration Profile for Cu_2O Surface Prepared As Indicated by Table 9.

SOLAR CELLS - COPPER-TO-OXYGEN RATIO VS DEPTH FOR Cu_2O SAMPLE

Figure 13

Copper-To-Oxygen Concentration Ratio vs. Depth For Cu_2O Substrate. Sample 1 Was Prepared To Table 3 And Sample 2 Was Prepared Without Steps 5, 6, 7, and 8 Of Table 3.

Table 9

 Cu_2O SURFACE PREPARATION PROCEDURE

STEP NO.	OPERATION
1.	Etch 5 minutes in HBF_4 .
2.	Rinse in DH_2O .
3.	Soak 1 minute in methanol with final 20 seconds in ultrasonic cleaner.
4.	Soak $1\frac{1}{2}$ minutes in 2% Br:methanol solution with final 30 seconds in ultrasonic cleaner.
5.	Repeat step #3.
6.	Repeat step #4.
7.	Repeat step #3.
8.	Soak 1 minute in warm ($40-45^\circ\text{C}$) 2% Br:methanol solution.
9.	Repeat step #3.
10.	Repeat step #3.
11.	Rinse in DH_2O .
12.	Blow dry with N_2 .

profile is given in Figure 12, and which was prepared according to the procedure in Table 9. Sample 2 was prepared as substrates used for devices early in this program. In particular, the early preparation procedures omitted steps 5 through 9. The difference in surface region composition for the two samples is remarkable. The surface of Sample 1 is clearly more favorable for solar cell fabrication.

Cu/Cu₂O cells fabricated with improved surface preparation has resulted in significantly improved performance. In particular, a current mechanism has been identified which is characterized by J_0 -values in the 10^{-9} to 10^{-8} A/cm² range; and $n \approx 1$. These values of J_0 are too low for a Cu/Cu₂O Schottky barrier, for which the expected value of J_0 is 4.7×10^{-7} A/cm². It appears that an interfacial region is having a positive impact on device parameters. One possible interfacial layer is CuBr. To assist us in device modeling, the surface of Sample 1 was examined very carefully. Very low levels of Cl, Br, and carbon were found on the first monolayer only. The evidence for bromine is described by Figure 14. A line spectrum taken on the surface indicates the presence of bromine, while a line spectrum taken after 15 seconds of milling (≈ 1 monolayer) does not indicate bromine. A surface coverage on the order of 0.1% is estimated for the bromine.

Electrical and optical characterization indicates that an interfacial layer exists in Cu-Cu₂O cells. The most likely interfacial layer would appear to be CuBr. The results of Auger analysis does not support such a model, however. We still regard an interfacial layer of CuBr, or CuBr_xO_y, to be a reasonable possibility. The Auger line observed for bromine is near 1400 eV, a region for which signal detection is relatively difficult. Bromine compounds readily dissociate when bombarded by ions or energetic electrons. Further investigation are underway.

5.3 Cu-Cu₂O MIS Cells

Significant progress has been made with Cu-Cu₂O frontwall cells, which appear to have an interfacial layer. After completing the surface preparation described in the last section, nineteen circular cells are formed on a Cu₂O substrate which is approximately 2 cm. in diameter, and 0.05 cm. thick. A picture of a Cu₂O substrate with nineteen devices formed

(A)

(B)

Figure 14 Auger Electron Line Spectrum For Bromine. (A) Taken On As Received Surface; (B) Taken After 15 Seconds Of Milling.

on it is shown in Figure 15. The diameter of an individual cell is 2.9 mm (.113 in.). Since the cell diameter is much larger than the minority carrier diffusion length, results obtained for cells of this size are significant.

5.3.1 Illuminated I-V Characteristics

The best results obtained to date are described in Figure 16. Based on total cell area, the efficiency and short-circuit current are 1.62% and 7.69 mA/cm^2 , respectively. An estimate of the area shadowed by the point probe was made by taking a picture. The shadowed region is estimated to be $\geq 8\%$ of the total area. Conservative estimates of values for active-area efficiency and short-circuit current are 1.76% and 8.33 mA/cm^2 . The short-circuit current can be corrected for series resistance effects to obtain the true J_{PH} . One finds $J_{PH} = 8.5 \text{ mA/cm}^2$. To our knowledge, these values of efficiency and photocurrent are the largest values ever reported for Cu_2O cells. Several cells have had efficiencies $> 1.5\%$, and photocurrents in excess of 7.5 mA/cm^2 .

5.3.2 Electro-Optical Characterization

To assist in determining an appropriate model for the $\text{Cu-Cu}_2\text{O}$ cells, I-V analyses versus temperature, and photoresponse measurements have been conducted. These studies indicate that an interfacial layer exists at the $\text{Cu-Cu}_2\text{O}$ interface which provides an effective barrier height on the order of 0.95 eV. Two current mechanisms contribute to current-voltage characteristics; a tunneling mechanism which is dominant at low voltages, and a component dominant at higher voltages which involves majority carrier transport over the 0.95 eV barrier.

Figure 17 shows typical results for transformed dark I-V characteristics of an individual cell. In particular, measured current is plotted against the junction voltage (V_j). Two current mechanisms are operative, one in the voltage range of 0 to 0.3 Volts and another in the range of $V_j > 0.3$ Volts, where $V_j = V - R_s I$, V being the applied voltage. The dark current-voltage characteristics have been interpreted in terms of the following expression:

Figure 15. Picture of Cu₂O Substrate with Small Area Cells.

SOLAR CELLS - Cu-Cu₂O MIS CELL PERFORMANCE

CELL 79FP58 - 13

STRUCTURE: Cu/CuBr/Cu₂O

Cu Layer - 83 Å

SiO AR - 700 Å

CELL AREA = .065 cm²

ILLUMINATED CHARACTERISTICS

AM1 SIMULATION

ILLUM AREA .060 cm²

T = 28°C

	BASED ON TOTAL AREA	BASED ON ACTIVE AREA
$J_{SC} \left(\frac{\text{mA}}{\text{cm}^2} \right)$	7.69	8.33
EFF (%)	1.62	1.76

Cu₂O MIS SOLAR CELL CHARACTERISTICS

Figure 16. Cu-Cu₂O MIS Solar Cell Characteristics.

SOLAR CELLS - DARK I-V ANALYSIS FOR Cu-Cu₂O MIS CELLS

Figure 17. Current-Voltage Analysis of Cu-Cu₂O Cell.

$$I = I_{01} \left[\exp(B_1 V_j) - 1 \right] + I_{02} \left[\exp\left(\frac{V_j}{n_2 kT}\right) - 1 \right] + V_j / R_{SH}$$

where

$$V_j = V - R_S I$$

V = Voltage Across Cell

I = Current through Cell

The high voltage mechanism is characterized by $J_{02} \approx 10^{-9} \text{ A/cm}^2$. It should also be noted that $n_2 \approx 1$. R_{SH} was determined to be $100 \text{ k}\Omega$ and R_S had a value of $185 \text{ }\Omega$ for this cell. If the cell area were 1 cm^2 instead of $.065 \text{ cm}^2$, R_S would be $\approx 12\Omega$. The theoretical value of J_0 for a Cu/Cu₂O Schottky barrier is $4.0 \times 10^{-7} \text{ A/cm}^2$ assuming the hole effective mass is $0.84 m_0$. Therefore, results of the I-V analyses provide indirect proof of a MIS structure. The effective barrier height is on the order of 0.94 eV . We tentatively identify the I-layer as one involving CuBr. However, due to the apparent low surface concentration of Br, the increased built-in voltage could partially be due to fixed charge at the interface.

Table 6 lists results for four separate cells. The analyses were carried out with a computer code, whereas, the analysis for cell 79FP61-4 (Figure 17) was done without the aid of computer analysis. It appears values are typically in the 10^{-9} A/cm^2 range, and $n_2 \approx 1.15$. Results are given for two pairs of cells in Table 10, one pair belonging to substrate 14 and another belonging to substrate 15. One of each pair had a good fill-factor while the other cell had a poor fill-factor. For example, cell 80FP14-6 exhibited very good characteristics, while 80FP14-15 did not. Similarly, 80FP15-9 was a "good" device and 80FP15-15 a relatively poor device. The "good" and "poor" devices are typically distinguished by values of R_{SH} and J_{01} . Investigations are underway to determine the cause for such differences to occur on the same substrate.

I-V characteristics have been investigated as a function of temperature in an effort to further understand the two current mechanisms. Table 11 lists I-V parameters determined for cell 80FP14-6 at various temperatures. The absolute error, averaged over approximately 15 data points is indicated.

Table 10
I-V PARAMETERS FOR Cu-Cu₂O CELLS

CELL	SUBSTRATE RESISTIVITY (Ω -cm)	TEMPERATURE ($^{\circ}$ C)	J_{o1} (A/cm ²)	B_1	J_{o2} (A/cm ²)	n_2	R_S (Ω)	R_{SH} (k Ω)
80FP14-6	319	23.4	9.75×10^{-6}	12.9	4.18×10^{-9}	1.13	130	20.6
80FP14-15	319	24.2	8.25×10^{-4}	9.09	8.67×10^{-9}	1.15	99.3	6.47
80FP15-9	175	23.9	7.95×10^{-5}	6.78	11.1×10^{-9}	1.09	90.6	41.7
80FP15-15	175	23.9	1.15×10^{-4}	6.03	9.36×10^{-9}	1.08	91.0	4.39

Table 11
I-V PARAMETERS FOR CELL 80FP14-6

TEMP. (°k)	B ₁	J ₀₁₂ (A/cm ²)	n ₂	J ₀₂₂ (A/cm ²)	R _s (Ω)	R _{SH} (kΩ)	AVE. ERROR (%)
321	13.8	1.63 x 10 ⁻⁵	1.08	2.92 x 10 ⁻⁸	111	9.21	0.58
303	11.3	2.46 x 10 ⁻⁵	1.12	8.58 x 10 ⁻⁹	122	8.38	0.14
297	12.9	9.75 x 10 ⁻⁶	1.13	4.18 x 10 ⁻⁹	130	20.6	1.00
282	12.8	7.29 x 10 ⁻⁶	1.14	1.08 x 10 ⁻⁹	147	27.6	0.96
271	12.3	5.72 x 10 ⁻⁶	1.19	5.16 x 10 ⁻¹⁰	166	43.1	0.53
255	11.5	4.32 x 10 ⁻⁶	1.25	1.33 x 10 ⁻¹⁰	209	55.2	1.56
242	13.9	1.13 x 10 ⁻⁶	1.16	5.05 x 10 ⁻¹²	270	85.8	1.50
223	13.4	5.00 x 10 ⁻⁷	1.31	2.14 x 10 ⁻¹²	438	200.	1.70

The parameter n_2 is constant and near unity, suggesting either a MIS behavior or some mixture of recombination current and thermionic emission current. The two current mechanisms are discussed further below.

The low voltage current component of cell 80FP14-6 is plotted for four temperatures in Figure 18. In particular, $I_{o1} \exp(BV_j)$ is plotted versus V_j , where

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

The parallel structure of the lines is a result of B_1 being essentially constant with temperature. Thus, the low voltage component appears to be a tunneling mechanism.

A plot of J_{o1} vs. $1000/T$ for this cell is given in Figure 19 on a semi-log scale. J_{o1} can be written as

$$J_{o1} \sim e^{-\frac{\epsilon}{kT}}$$

Thus, the tunneling mechanism can be interpreted as a thermally activated process. The activation energy for cell 80FP14-6 is 0.311 eV. Results for cell 80FP14-15 on the same substrate are also shown in Figure 19. Its activation energy is .382 eV. Analyses have been conducted for numerous devices. All exhibit the low voltage mechanism, and are characterized by $\epsilon \sim 0.3$ to 0.4 eV. It should be noted that the magnitude of J_{o1} varies considerably from cell to cell, being low in the more efficient devices.

Consider the high voltage current mechanism. This component can be interpreted in terms of modified Schottky barrier theory,⁸ namely,

$$I_2 = I_{o2} \left[\exp\left(\frac{V_j}{n_2 kT}\right) - 1 \right]$$

$$J_{o2} = A^* T^2 e^{-\chi_v} e^{\frac{1}{2} \phi_b} e^{-\phi_{BP}/kT}$$

$$n_2 = 1 + \alpha$$

CELL 80FP14-6

	T (°K)	R _S (Ω)	R _{SH} (kΩ)	J ₀₁ (A/cm ²)	B ₁
○	321	111	9.21	1.63 x 10 ⁻⁵	13.8
△	282	147	27.6	7.29 x 10 ⁻⁶	12.8
●	255	209	55.2	4.32 x 10 ⁻⁶	11.5
□	223	438	200.	5.00 x 10 ⁻⁷	13.4

Figure 18. Transformed I-V Characteristics for Low Voltage Current Mechanism of Cell 80FP14-6.

Figure 19. J_{01} vs. $1000/T$ for Cells on Substrate 80FP14.

$$\phi_{BP} = \gamma\phi_{B0} + (1 - \gamma)\phi_0 + \Delta\phi_{FC}$$

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

$$\alpha = (.1808)\left(\frac{D_s \delta}{K_i}\right)$$

$\Delta\phi_{FC}$ = Incremental change in ϕ_{BP} due to fixed charge at interface.

D_s = Density of surface states (10^{13} cm^{-2})

K_i = Relative dielectric constant of interfacial layer.

χ_v and δ are interfacial layer parameters as defined by Figure 20. Their units are eV and Å, respectively.

The high voltage current mechanism is due to holes thermionically emitted over the built-in barrier, and which tunnel through the interfacial layer. Figure 21 illustrates the two current mechanisms. As noted above, J_{o2} values clearly indicate that the effective barrier is on the order of 0.95 eV, much larger than the theoretical value for the Cu-Cu₂O contact. The difference can be due to the tunneling factor, effects of fixed charge, or both. The behavior of J_{o2} vs. T^{-1} can indicate an appropriate model.

J_{o2}/T^2 is plotted in Figure 22 versus $1000/T$ on a semilog scale. The slope of the straight lines indicate ϕ_{BP} , while the intercept as $1000/T$ goes to zero gives $A \cdot \exp(-\chi_v^{1/2} \delta)$. The effective mass of holes in Cu₂O has been reported to be $0.84 m_0$.⁹ Thus, $A \approx 101$. Values determined for ϕ_{BP} and $\chi_v^{1/2} \delta$ are given in Figure 22. Typically, $n_2 \approx 1.15$, implying $\alpha = 0.15$ and $\gamma = 0.87$. Letting ϕ_{B0} be 0.70, the values of ϕ_{BP} for cells 80FP14-6 and 15 can be interpreted in terms of different values of ϕ_0 or $\Delta\phi_{FC}$. Both parameters, of course, relate to the surface of Cu₂O. At this point, the only conclusion that can be made is that an interfacial layer appears to exist, and that, possibly, fixed charge may exist at the interface.

Further information is obtained from the barrier height determined from long wavelength photoresponse. Figure 23 shows results obtained for several cells. The barrier height determined in this manner is

Figure 20. Equilibrium Electron Band Diagram for p-MIS Cell.

Figure 21. Proposed Current Mechanisms Characterized by J_{01} and J_{02} .

Figure 22. J_{02}/T^2 vs. $1000/T$ for Cells on Substrate 80FP14.

Figure 23. Long Wavelength Photoresponse for Cu-Cu₂O Cells.

typically ≈ 0.95 eV. Since the photocurrent obtained in this measurement is due to electron transitions in the metal and subsequent hole injection into the valence band of Cu_2O , we interpret the barrier height to be

$$[\phi_B]_{PH} \approx \phi_{BP} + \chi_V$$

As a result, one can estimate χ_V by combining the J_{O2} vs. T^{-1} and long wavelength photoresponse studies. Values for the barrier height, and interfacial parameters for several cells are given in Table 12.

5.3.3 Implications Concerning Cu_2O Solar Cell Efficiency

The results of electro-optical characterization of Cu- Cu_2O cells have significant implications concerning the potential efficiency of Cu_2O . First, a tunneling current mechanism has been identified which varies considerably in magnitude. If this mechanism can be associated with substrate microstructure, impurities at the surface, or processing steps, it is quite likely that this current component can be eliminated. Elimination of the low voltage mechanism would result in Cu- Cu_2O solar cell efficiencies of 3%. Cell efficiencies can be further improved by increasing J_{PH} and improving the junction associated with the high voltage current mechanism.

If we assume that the tunneling mechanism can be essentially eliminated, and J_{PH} increased to 12 mA/cm^2 , then the task of primary importance concerns the achievement of an improved junction with a lower J_{O2} . Identification of the cause of the tunneling current mechanism is very important; otherwise, the benefits of an improved J_{O2} would never be realized.

There are several possible approaches to an improved junction. Clearly, any successful approach must involve material components compatible with Cu_2O . The ultimate efficiency of the Cu- Cu_2O MIS cells discussed in this section depends upon χ_C and whether fixed positive charge can be placed at the interface. If χ_C were near zero, then δ could be increased until J_{O2} is reduced several orders of magnitude. Fixed charge introduced in the I-layer would also yield a much lower J_{O2} .

Calculations of Cu- Cu_2O solar cell efficiency were carried out assuming

Table 12
BARRIER HEIGHT AND CALCULATED
INTERFACIAL-LAYER PARAMETERS*

CELL	ϕ_{BP} (eV)	$\chi_v \frac{1}{2} \delta$	$(\phi_B)_{PHOTO}$ (eV)	χ_v	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

* (i) ϕ_{BP} and $\chi_v \frac{1}{2} \delta$ determined from J_{O2} vs. T data, assuming

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

(ii) $(\phi_B)_{PHOTO}$ determined from long wavelength photoresponse.

(iii) χ_v and δ determined from values for $(\chi_v \frac{1}{2} \delta)$ and assuming

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

fixed charge can be incorporated in the interfacial layer. Figure 24 describes these studies. AM1 efficiency is plotted versus fixed charge density, assuming $J_{PH} = 8, 10, 12, \text{ and } 14 \text{ mA/cm}^2$. Calculated values of J_0 are also plotted. These calculations were carried out assuming

$$\phi_{BP} + \chi_V^{1/2} \delta = 0.96 + \Delta\phi_{FC} \text{ eV}$$

and
$$\Delta\phi_{FC} = \frac{N_{FC} \delta}{2K_i} \times 10^{-15} \text{ eV}$$

where $N_{FC} = \text{Fixed charge (cm}^{-2}\text{) per unit area}$

$\delta = \text{Interfacial layer thickness (\AA)}$

$K_i = \text{Relative dielectric constant}$

These results indicate that an inversion layer cell could approach the 8 to 10% range if approximately 3% surface coverage with fixed positive charge can be achieved.

5.4 Other Solar Cell Studies

Two other solar cell structures were examined during this contract, namely, $\text{Cu/SiO}_2/\text{Cu}_2\text{O}$ MIS structures and $\text{ZnO/Cu}_2\text{O}$ heterojunctions. A brief discussion of the results obtained follows.

5.4.1 Cu/SiO₂/Cu₂O MIS Cells

This study was motivated partially because we had previously fabricated a $\text{Cu/SiO}_x/\text{Cu}_2\text{O}$ cell which produced $V_{OC} = 0.5 \text{ Volts}$. If a 20 Å SiO_2 layer could be deposited onto Cu_2O , then one has a choice of several metals that can be deposited to complete the structure, and which would theoretically yield a high efficiency.

The most difficult step in fabricating the device is, of course, that of depositing a fairly uniform, 20 Å SiO_2 interfacial layer. The interfacial layer was formed by depositing SiO in the presence of oxygen (10^{-5} torr). Any excess silicon will reduce the Cu_2O resulting in excess copper. These comments concerning the difficulties associated with formation of an SiO_2 I-layer also apply to other candidate I-layers which must be deposited. However, it is clear that on a few occasions, a reasonable

Figure 24. Calculated Cu-Cu₂O Cell Efficiency with Fixed Charge
 Assuming $K_i = 1$ and $\delta = 20 \text{ \AA}$.

interfacial layer was obtained, since MIS cells based on an SiO_2 I-layer produced enhanced values of V_{OC} .

Table 13 summarizes results obtained with $\text{Cu/SiO}_2/\text{Cu}_2\text{O}$ cells. The preheat step refers to heating the Cu_2O in vacuum prior to SiO_2 deposition. The pressure level was typically in the low 10^{-6} torr. range. The most interesting results were those obtained for cell 79FP31 and 79FP31A. These cells refer to devices made with the same Cu_2O substrate. First, 79FP31 was fabricated with an SiO_2 layer of 16 Å. A V_{OC} -value of 0.19 Volts was obtained, similar to that typically obtained for a $\text{Cu/Cu}_2\text{O}$ Schottky barrier on highly doped material. The substrate was then polished again and a new device fabricated with a 23 Å SiO_2 I-layer, namely 79FP31A. The V_{OC} -value in this case was 0.365 Volts. This enhanced voltage appears to be a result of the interfacial layer. Subsequent attempts to fabricate an SiO_2 based MIS structure were unsuccessful.

Our experience with MIS cells based on vacuum deposited I-layers suggests that this approach may be very difficult to control adequately. The most successful MIS cell developments have been based on thermally grown oxide layers on Si and GaAs. More generally, the best approaches to forming I-layers in MIS cells have involved film growth by chemical reaction.

5.4.2 $\text{ZnO/Cu}_2\text{O}$ Heterojunctions

Cells were fabricated by reactively sputtering ZnO onto Cu_2O substrates. A thickness monitor was not available in the sputtering system, but the ZnO layers were thick enough to be visible. Copper contacts were deposited on the ZnO layers. Although an open-circuit voltage of 0.42 Volts was achieved, in one case cells exhibited poor current-voltage characteristics. In particular, significant cross-over effects were observed, suggesting a high density of interface states.

After fabricating these devices, new ZnO sputtering fixturing was designed and constructed. In particular, an axially arranged system was built so that the substrate could be covered prior to deposition. No further efforts have been devoted to this work since rebuilding the sputtering system.

Table 13

RESULTS FOR Cu/SiO₂/Cu₂O MIS CELLS

CELL	CELL AREA (cm ²)	PRE- HEAT TEMP. (°C)	Cu THICK- NESS (Å)	SiO ₂ THICK- NESS (Å)	R _S (Ω)	R _{SH} (Ω)	J _{SC} (mA/cm ²)	V _{OC} (VOLTS)
79FP30A	.185	306	91	23	550	3500	0.45	0.35
79FP31	1.5	280	98	16	5.1	2000	5.01	0.19
79FP31A	.185	306	91	23	35	9600	3.78	0.37
79FP32	.185	-	95	25	40	9600	0	0
79FP33	.185	459	97	18	200	617	1.62	0.12
79FP34	.135	461	87	14	250	2950	3.70	-0.20

6. FUTURE WORK

Future efforts should concentrate on improvement of Cu_2O material quality, increasing cell photocurrent and developing a junction with which significantly increased voltages can be obtained. To achieve these goals, the following four areas will be pursued:

- (i) Growth of Cu_2O Substrates and Films;
- (ii) N-Type Semiconductor Films;
- (iii) Photocurrent Studies;
- (iv) Solar Cell Fabrication and Characterization.

6.1 Growth of Cu_2O Substrates and Films

Efforts concerning growth of Cu_2O and substrate fabrication will consist of further work concerning thick substrates and exploratory studies regarding growth of Cu_2O appropriate for a thin film cell. Current fabrication of thick Cu_2O substrates often results in wafers with narrow channels which extend from one face to the other. These channels clearly can produce high values of shunt conductance and possibly reduce the minority carrier diffusion length. The microstructure of Cu_2O samples prepared by total oxidation of copper discs will be studied in further detail. Effects of material processing steps upon Cu_2O microstructure and subsequent impact on device properties will be emphasized.

Approaches to growth of thin films of Cu_2O will be investigated, as time permits. The following approaches will be considered: partial oxidation of copper; total oxidation of a copper film; sputtering of Cu_2O . The most desirable approach would appear to be one which is based on partial oxidation of copper. Relatively large grain polycrystalline Cu_2O films can be grown on copper substrates in a matter of minutes. The backwall diode that exists between the Cu_2O and mother copper must be eliminated, however. The possibility of utilizing a 10 μm to 20 μm film of Cu_2O grown by partial oxidation of a copper substrate will be examined. Deposition of a copper film and subsequent oxidation of the film will also be investigated. Such a film would most likely be used by forming the Cu_2O layer onto an n-type semiconductor which can tolerate the oxidation step, such as ZnO . Cu_2O films can be sputtered by RF sputtering techniques. Preliminary

studies also indicate that Cu_2O can be reactively sputtered.

6.2 N-Type Semiconductor Films

Reactively sputtered or MBE deposited ZnO , chemically formed CuBr and deposited Tl_2O_3 all appear to be promising approaches to forming an n-type layer on Cu_2O . Each of these will undergo preliminary evaluation, and then they will be investigated according to the determined priority.

ZnO films have been deposited n-type and cells have been made exhibiting photovoltaic properties. This approach may present some difficulties, however, since free Zn will reduce Cu_2O . Copper-halide films can be easily formed on Cu_2O and, therefore, may constitute a straight forward approach to obtaining an n-type, large band gap film on Cu_2O . Free energy calculations concerning metals in contact with Cu_2O indicate that most should reduce Cu_2O . Thallium is the only metal with a low work function that will not reduce Cu_2O . Thus, not only is a $\text{Tl-Cu}_2\text{O}$ junction worthy of examination, but $\text{Tl}_2\text{O}_3/\text{Cu}_2\text{O}$ junctions should be investigated. It would seem reasonable that Sn-doped Tl_2O_3 could be deposited as an n-type material.

6.3 Photocurrent Studies

Photocurrent studies will involve two aspects, photoresponse measurements and analysis, and efforts to continually demonstrate increased values of photocurrent. Frontwall $\text{Cu/Cu}_2\text{O}$ cells will be utilized for a continuing investigation of internal photoresponse. Thick substrates will be used so that cells may be assumed semi-infinite, and thus amenable to analysis. It is desirable to understand the role of exciton absorption concerning cell photoresponse. Thus, investigations of the internal photoresponse of $\text{Cu-Cu}_2\text{O}$ cells will continue in an effort to determine approaches to material processing which can yield larger values of J_{PH} .

As further understanding of the internal photoresponse is developed, it is expected that S_λ will increase. In particular, it is expected that the potential photocurrent for any given Cu_2O structure will increase. $\text{Cu/Cu}_2\text{O}$ cells will continue to be fabricated for photocurrent demonstration. As heterojunction device quality improves, these cells will be used for photocurrent demonstration. It is anticipated that photocurrents of

10 mA/cm² and 11 mA/cm² will be obtained during the next year with Cu/Cu₂O cells.

6.4 Solar Cell Fabrication and Characterization

Solar cells based on MIS and heterojunction structures will be investigated. Cells will be characterized by conducting both structural and electro-optical analyses.

MIS cells refer to devices which have an interfacial layer between Cu₂O and the front metal collector. The flexibility associated with such a structure is particularly important for this work. The interfacial layer may be a compound or a region incorporating fixed positive ions. The latter concept will be seriously considered. A layer containing positive charge would yield an enhanced barrier height, and yet still be compatible with a copper front contact.

Investigations of MIS cells will involve further studies of the Cu-Cu₂O cells discussed in Section 5. Two approaches for achieving enhanced barrier heights will be pursued: (i) utilization of a CuBr interfacial layer as part of a Cu/CuBr/Cu₂O MIS structure; (ii) incorporation of positive ions at the interfacial region. Clearly, an approach based on a combination of these may also be possible. Copper will continue to be used as the metal collector for approaches (i) and (ii). In principle, it appears that barrier heights on the order of 1.2 eV, or J₀-values on the order of 10⁻¹³ to 10⁻¹⁴ A/cm², can be achieved even though copper is utilized as the metal contact. As noted in Section 5, the density of ions on the surface must be approximately 10¹² to 10¹³ cm⁻² to achieve the required barrier height.

The three heterojunction structures, ZnO/Cu₂O, CuBr/Cu₂O, and Tl₂O₃/Cu₂O all appear promising. Efforts toward each approach could constitute a significant program. As a result, some preliminary investigations may be necessary before a single approach can be selected.

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APPENDIX A
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APPENDIX B
LIST OF PUBLICATIONS

Quarterly Progress Reports, "Investigation of Solar Cells Based on Cu_2O ," Reports DOE/ET/23006-1, -2, and -3.

"Investigation of Cu_2O Solar Cells," Conf. Rec. 14th IEEE Photovoltaic Spec. Conf., page 462, January, 1980.