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MASTER

CUPROUS OXIDE PHOTOVOLTAIC CELLS

Fourth Quarterly Technical Progress Report

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I. INTRODUCTION

The previous work on this project was devoted to a study of MIS cells and heterojunction cells with Cu_2O . In particular the junctions were studied by Auger techniques to detect possible chemical changes at the interface. It was found that some preparation conditions could produce heterojunctions without chemical degradation. In the last quarter, work was initiated on the effect of impurities in the starting Cu on the properties of the Cu_2O and Cu_2O solar cells. Methods of measuring diffusion length were explored. In this report a further examination of impurities in the Cu is presented. Some additional details on the $\text{CdO}/\text{Cu}_2\text{O}$ heterojunction are given. The measurement of diffusion length by a photocurrent method is described and some results are given.

II. DOPING AND EFFECT OF IMPURITIES IN Cu_2O

A. Purpose and Background

The purpose of this phase of the research is to study the effects of impurities in Cu_2O as they might arise from impurities in the starting Cu. As in any semiconductor, many impurities would be expected to have some effect; some would be beneficial as dopants, and others would be harmful, e.g. degrade the lifetime, or contribute interface states, etc. When Cu_2O rectifiers were produced commercially, it was known that great care had to be exercised in the selection of the grade of Cu and the processing of the Cu because the rectifier properties depended strongly on these factors.

B. Phase Diagrams

Usually the additions are expected to be made at $\sim 0.01\%$ to 0.1% level in the initial screening, and most impurities could be expected to be soluble at this level. Nevertheless it is possible to verify this for a number of the elements from the phase diagrams. Several relevant diagrams are given here (1) in Figures 1, 2, and 3.

Most of the elements of probable interest appear to be sufficiently soluble. Silicon, for example, is soluble to the extent of 5.3% (weight percent), and a number of others are similar. Some are rather low in solubility, such as Se at 0.04%, and Tl at 0.9%. Some elements are miscible with Cu in all proportions such as Ni, shown here, as well as Au, Mn, Pd, Pt, and Rh, which are not shown. Several have segregation coefficients ($K = C_S/C_L$) greater than one, i.e., Ni, Co, Fe, Rh, Pt, Pd, Ir, so that in zone refining these would not be swept to the far end but might accumulate at the front end of the rod. It is notable that Ag has limited solubility in Cu and forms a simple eutectic. In view of its close chemical similarity, one might have expected it to be soluble in all proportions. Silver is a very common contaminant in Cu.

C. Experimental Methods

Procedure: The procedure for casting Cu with added impurities was described in the previous Quarterly Report. A Cu slug with the impurity inserted in a drilled hole is melted in vacuum by induction heating and is allowed to flow into a graphite mold to form a bar on solidification. The bar is rolled into a long sheet, which is cut into short sections. These are oxidized to Cu_2O to be used for resistivity measurements and the preparation of photovoltaic cells.

Ag-Cu Silver-Copper

Be-Cu Beryllium-Copper

Al-Cu Aluminum-Copper

As-Cu Arsenic-Copper

Cd-Cu Cadmium-Copper

Cu-Ga Copper-Gallium

Cu-Fe Copper-Iron

Cu-In Copper-Indium

Cu-Mg Copper-Magnesium

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Apparatus: The apparatus was described in the text of the previous Quarterly Report. The apparatus is shown here in the accompanying illustrations. Fig. 4 is a general view of the apparatus, with the pedestal support in the middle, the induction power supply in the back (left) and the controller in the front (right). Fig. 5 shows the crucible mounted on the pedestal. The Cu slug is in the head space above the insert in the crucible. Fig. 6 shows the crucible enclosed in the Vycor tube and surrounded by the 10-turn work coil. Fig. 7 shows the graphite crucible, the slotted graphite insert, and the Cu ingot with a cap on the drilled hole. Fig. 8 shows the crucible being heated by the induction coil during a melting run. Fig. 9 is a picture of the rolling mill used to roll the cast Cu bar into sheet suitable for oxidation. Fig. 10 shows the crucible, insert, cast bar and the starting Cu slug.

Materials: In addition to the ASARCO high purity Cu (99.999+%) used in the initial experiments, high purity Cu starting materials from other suppliers were also tested. These were MARZ grade 99.999+% Cu from Materials Research Corp. and Gallard-Schlesinger 99.999+% Cu from Gallard-Schlesinger Chemical Co. The impurity addition were of reagent grade or best available.

Figure 4 General View of Apparatus.

Figure 5 Crucible in Pedestal.

Figure 6 Enclosed Crucible.

Figure 7 Crucible, Insert, and Cu Slug.

Figure 8 Crucible Being Heated.

Figure 9 Rolling of Copper.

Figure 10 Crucible, Insert,
Cast Bar, and Starting Copper.

D. Results

General: One impurity run is shown here as an example.

CdF ₂ II A ₁	1.8 cm
CdF ₂ II 01	6 cm
CdF ₂ II 02	6.5 cm
CdF ₂ II 03	6 cm
CdF ₂ II A ₂	1.5 cm
CdF ₂ II 04	5.5 cm
CdF ₂ II 05	6.2 cm
CdF ₂ II A ₃	4 cm

Weight of Cu + CdF₂ = 35.6406g

Weight of Cu = 35.6324

Weight of CdF₂ = 0.0082g

% CdF₂ = 0.022%

The rolled sheet was cut into strips
~ 6 cm long as shown on the left.

A₁, A₂ and A₃ were reserved for
chemical analysis.

Representative strips were oxidized
for resistivity measurement and for
photovoltaic cells. Results on CdF₂ II 01
were:

	ρ ($\Omega \cdot \text{cm}$)
CdF ₂ II 01 A ₁	814
CdF ₂ II 01 A ₂	454
CdF ₂ II 01 B ₁	150
CdF ₂ II 01 B ₂	208
CdF ₂ II 01 C ₁	133
CdF ₂ II 01 C ₂	140
CdF ₂ II 01 D ₁	114
CdF ₂ II 01 D ₂	130

	SAVED
CdF ₂ II 01	A
	B
	C
	D
	SAVED

At this stage, chemical analyses are not being made routinely. Some indication of the variation in the impurity content was obtained from the analysis of a Si-containing sample. The analysis was done spectrophotometrically by the heteropoly blue method(10). The calculated added concentration was 0.05% (508 ppm). The top of the rolled 42 cm strip was found to contain 718 ppm and the bottom 454 ppm, while a sample at 16 cm from the top had 618 ppm.

In the following results, the range of resistivity values is given and the photovoltaic results in the best cell made with a Cu top contact. The Cu_2O was made by oxidation of the Cu sheet in air at 1000°C and was not subjected to grain growth or other annealing.

ASARCO Cu with 0.05% Si: This material gave resistivities, ρ , from 202 to $1142 \Omega\cdot\text{cm}$. The best cell had $J_{\text{SC}} = 3.25 \text{ mA/cm}^2$ and $V_{\text{OC}} = 0.23 \text{ V}$. Some further data are given in Table I.

ASARCO Cu with 0.1% Si: This material gave ρ of 201 to $818 \Omega\cdot\text{cm}$. The photovoltaic results were not as good as those obtained with 0.05% Si yielding $J_{\text{SC}} = 2.25 \text{ mA/cm}^2$ and $V_{\text{OC}} = 0.185 \text{ V}$. Some additional data are given in Table II.

Gallard-Schlesinger Cu with 0.2% Si: The resistivity varied from 227 to $1.67 \times 10^4 \Omega\cdot\text{cm}$ and the best cell had $J_{\text{SC}} = 2.7 \text{ mA/cm}^2$ and $V_{\text{OC}} = 0.265 \text{ V}$. Some results are shown in Table III.

Gallard-Schlesinger Cu with 0.01% Se: The resistivity varied from 224 to 260 $\Omega \cdot \text{cm}$. The photovoltaic results were poor. Some results are given in Table IV.

Gallard-Schlesinger Cu with 0.018% Mg: The resistivity values ranged from 149 to 219 $\Omega \cdot \text{cm}$. The best cell had $J_{\text{sc}} = 1.4 \text{ mA/cm}^2$ and $V_{\text{oc}} = 0.135 \text{ V}$.

Gallard-Schlesinger Cu with 0.042% Cd: The resistivity varied from 172 to 368 $\Omega \cdot \text{cm}$. The best cell had $J_{\text{sc}} = 1.5 \text{ mA/cm}^2$ and $V_{\text{oc}} = 0.145 \text{ V}$. In general, the photovoltaic results were poor. Some results are given in Table V.

Gallard-Schlesinger Cu with 0.057% Tl: The resistivity was 172 to 269 $\Omega \cdot \text{cm}$. As shown in Table VI, the photovoltaic results were poor.

Gallard-Schlesinger Cu with 0.05% CdF_2 : The resistivity varied from 140 to 1980 $\Omega \cdot \text{cm}$. Some cell data are given in Table VII.

Gallard-Schlesinger Cu with 0.05% MgF_2 . The MgF_2 did not dissolve completely. The resistivity ranged from 181 to 1200 $\Omega \cdot \text{cm}$. The best cell gave $J_{\text{sc}} = 2.96 \text{ mA/cm}^2$ and $V_{\text{oc}} = 0.255 \text{ V}$. The cell data are given in Table VIII.

MARZ Cu with 0.022% CdF_2 : This material gave ρ from 114 to 814 $\Omega \cdot \text{cm}$, and a best cell of $J_{\text{sc}} = 2.75 \text{ mA/cm}^2$ and $V_{\text{oc}} = 0.21 \text{ V}$. Some data are given in Table IX.

MARZ Cu with 0.022% Cl: The chloride was added as anhydrous cuprous chloride, CuCl . This material gave ρ with 166 to 676 $\Omega \cdot \text{cm}$ and a best cell of $J_{\text{sc}} = 2.18 \text{ mA/cm}^2$ and $V_{\text{oc}} = 0.25 \text{ V}$. Some results are given in Table X.

TABLE I

Properties of Solar Cells Made from ASARCO Copper Doped with 0.05% Si

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{oc} (V)	J_{sc} (mA/cm^2)
1	300	0.22	3.20
2	320	0.23	3.25
3	250	0.17	3.20
4	318	0.11	2.60

TABLE II

Properties of Solar Cells Made from ASARCO Copper Doped with 0.1% Si

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{oc} (V)	J_{sc} (mA/cm^2)
1	201	0.185	2.25
2	415	0.11	1.4
3	264	0.07	1.5

TABLE III

Properties of Solar Cells Made from Gallard-Schlesinger Copper Doped with 0.2% Si

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{oc} (V)	J_{sc} (mA/cm^2)
1	525	0.265	2.70
2	227	0.205	2.50

TABLE IV

Properties of Solar Cells Made from Gallard-Schlesinger Copper Doped with 0.01% Se

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{oc} (V)	J_{sc} (mA/cm^2)
1	224	0.11	1.3
2	244	0.08	0.70

TABLE V

Properties of Solar Cells Made from Gallard-Schlesinger Copper Doped with 0.0424% Cd

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{OC} (V)	J_{SC} (mA/cm^2)
1	233	0.09	0.75
2	368	0.145	1.50
3	260	0.04	0.55

TABLE VI

Properties of Solar Cells Made from Gallard-Schlesinger Copper Doped with 0.0574% Tl

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{OC} (V)	J_{SC} (mA/cm^2)
1	269	0.05	1.8
2	172	0.025	1.00

TABLE VII

Properties of Solar Cells Made from Gallard-Schlesinger Copper Doped with 0.05% CdF_2

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{OC} (V)	J_{SC} (mA/cm^2)
1	271	0.295	2.70
2	178	0.140	2.70
2A	178	0.210	2.30

TABLE VIII

Properties of Solar Cells Made from Gallard-Schlesinger Copper Doped with 0.05% MgF_2

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{OC} (V)	J_{SC} (mA/cm^2)
1	402	0.115	2.25
2	362	0.280	2.75
3	290	0.255	2.96
4	467	0.250	2.30
4A	remade the cell	0.330	2.66

TABLE IX

Properties of Solar Cells Made from MARZ Copper Doped with 0.022% CdF₂

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{OC} (V)	J_{SC} (mA/cm ²)
1	206	0.09	2.75
2	195	0.155	3.30
3	-	0.21	2.75

TABLE X

Properties of Solar Cells Made from MARZ Copper Doped with 0.022% Cl

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{OC} (V)	J_{SC} (mA/cm ²)
1	421	0.22	2.25
2	-	0.25	2.18
3	-	0.175	2.25
4	-	0.170	1.75

TABLE XI

Properties of Solar Cells Made from MARZ Copper Doped with Iodide

Sample	ρ ($\Omega \cdot \text{cm}$)	V_{OC} (V)	J_{SC} (mA/cm ²)	%I
1	368	0.19	1.9	0.033
2	184	0.14	2.37	0.033
3	171	0.085	1.90	0.033
4	222	0.17	2.12	0.060
5	290	0.36	2.37	0.060
6	421	0.26	2.37	0.060

MARZ Cu with 0.033% I. The iodide was added as cuprous iodide, CuI.

This material gave ρ with 166 to 676 $\Omega\cdot\text{cm}$ and a best cell of

$J_{\text{SC}} = 1.9 \text{ mA/cm}^2$ and $V_{\text{OC}} = 0.19 \text{ V}$.

MARZ Cu with 0.6% I: This material had resistivities of 222 to 473 $\Omega\cdot\text{cm}$. The best cell gave $J_{\text{SC}} = 2.37 \text{ mA/cm}^2$ and $V_{\text{OC}} = 0.36 \text{ V}$. As shown in Table XI, the higher concentration of iodide may be beneficial.

Discussion: There is considerable scatter in the results, so that small differences cannot be used to distinguish trends. The resistivity values did not go below 100 $\Omega\cdot\text{cm}$. The photovoltaic results at best were 2-3 mA/cm^2 , occasionally slightly higher. The V_{OC} often was 0.2 to 0.3 V and occasionally higher, but frequently lower.

The sources of the scatter in the results are not known, and they could be due to accidental impurities in the commercial sources of the Cu or some part of the processing procedure.

Attempts were made to run blanks. The Gallard-Schlesinger Cu run through the entire procedure but with no purposely added impurities gave ρ of 161 to 384 $\Omega\cdot\text{cm}$ and a best cell of $J_{\text{SC}} = 1.7 \text{ mA/cm}^2$ and $V_{\text{OC}} = 0.16 \text{ V}$. The MARZ Cu gave ρ of 190 to 404 $\Omega\cdot\text{cm}$ and a best cell of $J_{\text{SC}} = 2.75 \text{ mA/cm}^2$ and $V_{\text{OC}} = 0.13 \text{ V}$. These were processed from the 3/4" ingots in each case.

The MARZ Cu is also available from the supplier in 1" strip of 0.020" thickness. This may or may not be equivalent to the MARZ material in the 3/4" rod form. The strip could be processed by us with much less handling and this was oxidized and processed into cells. After oxidation at 1000°C and without annealing, this tended to give somewhat higher resistivities, 10^4 to $10^5 \Omega\cdot\text{cm}$, as we previously obtained with OFE Cu, but sometimes lower

values were obtained, 1000-3000 $\Omega \cdot \text{cm}$ and as low as 500 $\Omega \cdot \text{cm}$. Again one might conclude that the variability is due to the Cu as supplied or some processing steps. It is possible to conclude that none of the impurities as added was able to lower the resistivity below 100 $\Omega \cdot \text{cm}$. Some impurities, perhaps accidental, can lower the resistivity below 10^4 $\Omega \cdot \text{cm}$, approaching 100 $\Omega \cdot \text{cm}$. If a dopant exists that can reduce the resistivity to 10 $\Omega \cdot \text{cm}$ or below, this could be seen by the present procedure.

The general procedures for introducing the impurities into the Cu have been developed and it is apparent that the impurities do have an important effect on the photovoltaic results. However it will be necessary to establish a more stable base line before definite conclusions can be drawn. We have in the past obtained J_{sc} up to 7-8 mA/cm^2 and V_{oc} up to 0.35-0.40 V and it should be possible to return to this condition.

III. HETEROJUNCTIONS

Due to the extended illness of the researcher concerned with heterojunctions, studies of new heterojunction structures were not initiated during this quarter. The Ion Tech sputtering apparatus was modified to accept mixtures of argon and oxygen, and preliminary testing was made of operations under these conditions. The tungsten filaments suffered a rapid burn out with oxygen presumably due to volatile tungsten oxides. This may also become a source of contamination of the system including the target material and eventually the samples. It maybe advisable to switch to another type of filament, e. g. platinum.

The Auger data on heterojunctions which have been stored in the computer memory, were reviewed with new procedures developed at General Motors Research Laboratories. The particular item of interest was the CdO/Cu₂O heterojunction as probed with the Cu MVV peak at ~ 57 eV. It was verified that the CdO/Cu₂O heterojunction prepared at room temperature showed no trace of Cu(I) at the junction. Therefore it can be affirmed that this is a true heterojunction, free from any reduction to Cu metal at the interface. This proves that in principle it is possible to prepare heterojunctions on Cu₂O under the proper conditions.

IV. MEASUREMENT OF DIFFUSION LENGTH, CAPACITANCE, AND JUNCTION PROPERTIES IN SCHOTTKY BARRIER CELLS

A. Introduction

It is desirable to increase the electron diffusion length, and the built-in potential in Cu/Cu₂O Schottky barrier solar cells in order to improve the conversion efficiency. To measure the diffusion length we have examined a photocurrent method which involves measuring the depletion width and the photocurrent at different reverse biases. The dielectric constant of Cu₂O

was also measured since this is required to obtain the depletion width. It was found that the photocurrent method is applicable to Cu_2O cells. Further studies with the method will be beneficial in providing a better understanding of Cu_2O and Cu_2O photovoltaic cells

B. Background

The photocurrent method used here for the measurement of the minority carrier diffusion length in Schottky barrier Cu_2O solar cells is similar to a method described by Logan, et al (2) for p-n junctions and applicable to both p and n type semiconductors. If it is assumed (a) that the lifetime of the carriers is much greater than their transit time across the depletion region and (b) that the generation rate of the carriers in the barrier region and its immediate vicinity is uniform, one can find that the device photocurrent is proportional to the sum of the depletion width and the minority carrier diffusion length. This expression is derived in a later section, and it is shown that, by varying the depletion width, W , one can measure the diffusion length. It is assumed that the measured photocurrent is due to band-to-band electron-hole generation in the semiconductor and that the participation of photoenergetic carriers from the metal to the semiconductor is negligible. This technique has been used by several other investigators including Smith and Abbott (3) for GaP and Baghdadi, et al (4) for Si.

C. Experimental Methods

Sample Preparation: Plates of Cu of the OFE and MARZ grades as well as some of the doped Cu samples developed in the impurity studies were oxidized completely to Cu_2O at 1000°C . No further annealing was used, such as those

utilized sometimes to promote grain growth or to improve the conductivity. The resistivities of the samples were from a few hundred to a thousand $\Omega \cdot \text{cm}$. The samples were ground, polished and etched in 8 M HNO_3 , and then were heat-treated and metallized in a vacuum by our normal procedures.

For the dielectric measurements, two circular gold electrodes were evaporated on the two sides of the samples, and some samples were provided with a guard ring also. The samples for the photocurrent measurements were coated with Au on the entire back surface and the front surface typically was a circular spot of Cu of $\sim 80 \text{ \AA}$ thickness and a few tenths cm^2 in area.

Capacitance Measurement. For the measurement of diffusion length, one must measure the depletion layer capacitance, which is of the order of nF. For the measurement of the dielectric constant of Cu_2O , one must measure the capacitance of a Au- Cu_2O -Au structure, which is of the order of pF for the geometrical dimensions of the samples used.

(a) Measurements in the nF Range. The electrical circuit used for measurements in the nF range is shown in Fig. 11.

Figure 11 Circuit for Measurement of Depletion Capacitance

For the measurement of the depletion capacitance, C_d , switch K_2 is connected, and K_1 is disconnected. The source signal is obtained from the reference channel of a Princeton Applied Research Model 126 Lock-in Amplifier. The signal across the resistance r ($r = 10 \Omega$) is not in phase with the source signal. In the Appendix it is shown that this signal consists of two components, one in phase and the other $\pi/2$ in advance of the source signal. The amplitudes of these two components $V(0)$ and $V(\pi/2)$ are given by

$$V(0) = \frac{V_0 r}{R_{sh} + R_s + R} \quad \text{and} \quad V(\pi/2) = \frac{C_d \omega R_{ch}^2}{(R_{sh} + R_s + R)^2} V_0 r$$

$V(0)$ and $V(\pi/2)$ can be measured at the output of the lock-in amplifier. In the above equations, ω is the angular frequency and V_0 is the amplitude of the source signal. It follows that $C_d = (R_{sh} + R_s + R) V(\pi/2) / \omega R_{sh}^2 V(0)$. Since the shunt resistance R_{sh} is not very high in our samples, less than $2.5 \text{ k}\Omega$, and also changes with the reverse bias, it is necessary to obtain accurate values for R_{sh} in order to obtain accurate values for C_d .

In previous measurements, values of R_{sh} were obtained from the slope of the I-V curve at reverse biases, but this method was found to be inaccurate. A better method is to replace the device with a standard resistance box and change the resistance to obtain the same value for $V(0)$ as with the device in the circuit. From the measured resistance, one obtains $R_{sh} + R_s$. The series resistance can be evaluated accurately from the slope of the I-V curve at high forward voltages.

(b) Measurements in the pF Range The circuit used for the measurement of the Au-Cu₂O-Au structures is shown in Fig. 12.

Figure 12 Circuit for Measurement of Capacitance for Dielectric Constant

In the Appendix, it is shown that

$$V(0) = V_o \frac{R_{sh}}{R + R_{sh}} \quad \text{and} \quad V(\pi/2) = -V_o \frac{R_{sh}^2 R C \omega}{(R + R_{sh})^2}$$

$$\text{where } C = \frac{(R + R_{sh})}{\omega R R_{sh}} \cdot \frac{|V(\pi/2)|}{V(0)}$$

$V(\pi/2)$ is nearly 100 times as large as $V(\pi/2)$ in the previous method. For this reason, this method is more accurate for the measurement of the very low capacitances.

Accurate values for R_{sh} can be obtained by using the external resistance box, as discussed before. Extra care must be taken in the measurement of $V(\pi/2)$ to exclude the effect of the dead capacitance, which is associated with the wiring and is of the same order of magnitude as the device capacitance.

Photocurrent Measurements. For the measurement of the photocurrent, the electrical circuit of Fig. 11 was used with switch K_1 connected and K_2 disconnected. The resistance r was 1Ω in this case. The illumination was obtained from

the output beam of a Bausch and Lomb monochromator, which was focussed on the Cu electrode of the front-wall cell after passing through a low bandwidth filter and a mechanical chopper with a frequency of about 300 Hz. The external signal for the reference channel of the lock-in amplifier was provided by a CdS photodiode irradiated with a beam of white light chopped with the same chopper. The area of the front Cu electrode was a few tenths of a cm^2 .

D. Results and Discussion

Dielectric Constant. The measurement of dielectric constant κ of samples of Cu_2O was carried out by measuring the capacitance C of the samples and applying the formula $C = \kappa \epsilon_0 A/d$, where ϵ_0 is vacuum permittivity, d is the sample thickness, and A is the effective area of the electrodes. All measurements were made at 5 kHz which is the same frequency used to measure the depletion capacitance. The measured values were found to vary from sample to sample, and even from one part to another of a given sample. The results for six samples, shown in Table XII, vary from 6.6 to 8.8. The average of 7.45 is slightly smaller than the value reported by Weichman (5).

TABLE XII

Sample	Dielectric Constant of Cu_2O (at 5 kHz)
DLF-Si-W	6.6
DLF-Cd-I	6.9
DLF-MgF ₂	8.8
AR-I-02	7.9
AR mIV-11	7.0
AR mIV-12	7.5

One sample was measured at different frequencies ranging from 1 kHz to 200 kHz. The results confirmed previous reports on the decrease of κ with increasing frequency. The value of 7.45 for κ was adopted for use in the measurement of the depletion width.

Electron Diffusion Length. Under monochromatic illumination by light of wavelength λ , the photocurrent, I_n , is due to electrons generated in the depletion layer of width W , and the electrons which are generated in the bulk beyond the edge of the depletion layer and which can diffuse to the depletion layer.

Thus, $I_n = A q \phi_0 (1-R) \eta \left[\int_0^W \exp(-\alpha x) dx + \int_W^l \exp(-\alpha x) \cdot \exp\left(-\frac{x-W}{L_n}\right) dx \right]$ (1) where q is the electronic charge, α is the absorption coefficient, ϕ_0 is the incident light intensity, R is the reflection coefficient, l is the sample thickness, W is the depletion layer thickness, L_n is the electron diffusion length and A is the sample active area.

For $l \approx 200 \mu\text{m}$, $L_n \approx 5 \mu\text{m} > W$, one can write $I_n = A \eta q \phi_0 (1-R) \left[1 - \frac{\exp(-\alpha W)}{1 + \alpha L_n} \right]$

In the wavelength region where $\alpha W \ll 1$, this gives

$$I_n = A \eta q \phi_0 (1-R) \frac{\alpha}{1 + \alpha L_n} (L_n + W) \quad (2)$$

The depletion width, W , was determined from measurements of the diffusion capacitance, $C_d = \kappa \epsilon_0 A/W$ at different reverse biases, using $\kappa = 7.45$, $\epsilon_0 = 1/(4\pi \times 9 \times 10^9) \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$, and A = junction area. The photocurrent, I_n , was also measured at the same reverse biases. The plot of I_n vs. W was extrapolated to $I_n = 0$ to yield $-L_n$ as the intercept. A suitable wavelength for the condition of $\alpha W \ll 1$ is 610 nm.

Fig. 13 shows a set of plots of I_n vs. W for different wavelengths using an undoped sample. The plots at 600 nm and 610 nm are straight lines up to $W = 0.9 \mu\text{m}$, corresponding to a reverse bias of 1 Volt. These give values of $0.4 \mu\text{m}$ for the electron diffusion length. As may be expected from equations (1) and (2), I_n vs W will not give a straight line at shorter wavelengths

Figure 13 Plots of Photocurrent vs. $\eta_{\text{depletion}}$ Width at several Wavelengths

where α is larger and for larger depletion widths where the condition $\alpha W \ll 1$ is not obeyed. This is shown in the 400 nm and 500 nm plots for $W > 0.4 \mu\text{m}$.

The electron diffusion length was measured for other samples with better J_{sc} and V_{oc} , and the results are given in Table XIII.

TABLE XIII

Sample	<u>Results of Diffusion Length Measurements</u>				Minimum observed for C_d vs. V_R
	V_{oc} (V)	J_{sc} (mA/cm ²)	L_n (μm)	V_{bi} (V)	
(1) AB-Si III 03 C	0.165	2.4	1.15	0.22	Yes
(2) AB-Si II 06 B	0.150	2.25	1.6	0.36	Yes
(3) DLF-MgF ₂ I	0.260	2.6	0.9	0.45	Yes
(4) AR-mIV 12	0.030	1.0	0.4	0.10	No
(5) AR-CuI I04	0.080	1.7	0.11	0.32	No
(6) DLF-Se III	0.140	1.7	-	-	Yes
(7) AR XX 06h	-	-	0.4	0.25	No
(8) DLF V III 24A	0.08	1.0	0.55	-	No

In this set of samples, the best value obtained for L_n was $1.6 \mu\text{m}$ for a silicon-doped sample. A systematic study will be undertaken to study the effect of different conditions of cell preparation on the resultant minority carrier diffusion lengths.

One possible explanation for the relatively low diffusion lengths in these samples is the small grain size in these samples and the relatively large area copper electrodes that were used. If the diffusion length is lower in the vicinity of the grain boundaries and if the electrodes spans a number of grain boundaries, then the measured L_n would be lowered, since it is a mean value of

the distributed L_n across the area.

Junction Properties. Values for the built-in potential V_{bi} for the various samples were obtained from plots of C_d^{-2} vs. V_R . Fig. 14 shows such a plot for an iodide-doped sample. The measured built-in potential is 0.32 V. These plots give straight lines provided the C_d is calculated using the values of R_{sh} obtained with the lock-in amplifier. If R_{sh} values obtained from the slopes of the I-V curves are used, the plots are often not straight lines. The values for the built-in potential for the samples are given in Table XIII. The highest value obtained was 0.45 V, for a MgF_2 -doped sample.

For some of the doped samples, except #5 in Table XIII, the measured C_d as a function of V_R decreased to a minimum and then showed an anomalous increase with increasing V_R . In the normal region of decreasing C_d , where the samples behave as the undoped samples, plots of C_d^{-2} vs V_R and I_n vs. W give straight lines from which L_n and V_{bi} were evaluated. The abnormal increase of C_d with increase in V_R is associated with a decrease in I_n with V_R for only short wavelengths. Fig. 15 shows this effect for a silicon doped sample, while Fig. 16 shows the normal type of behavior of C_d and I_n with V_R for an undoped sample.

As shown in Table XIII, for this set of samples, the samples which show the abnormal behavior of C_d vs. V_R also show the higher J_{sc} and V_{oc} . This may mean that there is some rearrangement of the impurity and defect levels in the band gap of Cu_2O or at the junction as a consequence of the addition of impurities. However, it will be necessary to study the effect further before a further understanding of the effect of impurities on cell performance can be developed.

Figure 14 Plot of $1/C^2$ vs. Reverse Bias Used to Determine Built-in Potential

Figure 15 Plots of Capacitance and Photocurrent vs. Reverse Bias for a Doped Sample Showing Anomalous Behavior

Figure 16 Plots of Capacitance and Photocurrent vs. Reverse Bias for an Undoped Sample Showing Normal Behavior

The work of this quarter was devoted to a development of the procedures for introducing impurities into the starting Cu to study their effects on the Cu₂O solar cell properties, some evaluation of heterojunctions by Auger analysis, and the development of procedures to measure the diffusion length in Cu₂O cells.

It is obvious that impurities do have an effect on the properties of Cu₂O solar cells, as might have been expected. The tentative conclusions are that the best cells are obtained with small amounts of silicon and that the halogens, F, Cl, I may be beneficial. Se, Tl, and Cd gave poorer cells. However it appears that some accidental impurities exist in the starting Cu or are introduced in the processing procedures, and this prevents more definite conclusions from being drawn at this stage. Some grades and lots of Cu on oxidation at 1000°C give Cu₂O with resistivities of 10^4 to 10^5 Ω·cm, and annealing at 500°C is required to reduce ρ to 100-200 Ω·cm. A number of doped samples give ρ of 100-200 Ω·cm and this could be useful in that the additional step of the 500°C anneal might be eliminated. No dopant was found that reduced ρ below 100 Ω·cm, although the present procedure was adequate to detect this.

The lack of good standards at this point is a handicap to detecting trends in the results, and it will be necessary to improve this situation. It is possible that the difficulty is due to variability in the starting Cu since the 99.999+% Cu which is used may contain up to 10 ppm of impurity. Amounts of Se and Te as low as 2 ppm have been shown (6) to be harmful in Cu₂O rectifiers. These are known contaminants in Cu, especially from sulfide ores. In fact Se and Te are chiefly obtained as by-products in the electro-refining of Cu. The quality of the graphite used for the crucibles is also

suspect, but we have used the best available UCAR grades, also used and recommended by ASARCO in the preparation of their 99.999+% Cu.

Thus in order to make the work on impurities more effective, it will be necessary to improve the materials and the procedures. We plan to monitor these aspects with better and more sensitive analytical procedures. If a commercial source of purer Cu cannot be located, we plan to purify Cu by zone refining (7) or electrorefining (8) or both.

While the doped Cu_2O was used as grown at 1000° in order to simplify the procedure, nevertheless a further anneal may be useful, i.e., an anneal at 500°C or slow cooling in a controlled atmosphere, and also a variation in the temperature and oxygen pressure during oxidation. This may reduce the degree of compensation by donors so that lower lying acceptor states can be revealed.

In summary, it is evident that impurities in the Cu can affect the properties of Cu_2O and Cu_2O solar cells in significant ways and it is important to identify the pertinent impurities and their effects.

The heterojunction work was temporarily delayed but remains an important part of this project. The critical factor is to verify whether a heterojunction has really been made or whether the photovoltaic response is due to a $\text{Cu}/\text{Cu}_2\text{O}$ Schottky barrier cell resulting from chemical reactions at the interface. It is important to monitor each case by methods such as high resolution Auger analysis. Such an analysis has shown that it is possible to prepare a true heterojunction, as exemplified by the case of the $\text{CdO}/\text{Cu}_2\text{O}$ heterojunction. Even in the case of junctions where reduction to Cu has occurred, it may be possible to reoxidize the Cu to Cu_2O by judicious heat treatment in controlled oxygen atmospheres or by anodization, or similar treatments. A broad investigation of heterojunctions on Cu_2O is planned,

especially with other oxide semiconductors, and a number of candidate materials remain to be tried.

The diffusion length is an important parameter to monitor in solar cells. Our previous work on the measurement of diffusion length in Cu_2O based on the surface photovoltage method was clouded by the fact that reliable data on the absorption coefficient in Cu_2O as a function of wavelength are not available. The current method under investigation involves the measurement of photocurrent while the width of the depletion layer is varied by reverse bias, and it does not depend on knowing the absorption coefficient accurately. The method appears to be satisfactory for determining the diffusion length in the Cu_2O solar cells. The work so far was mainly intended to establish the method, so that it will be available to study the effect of processing procedures and the quality of the Cu_2O on the diffusion length. Some current cells were measured and reasonable values for L_n were obtained. The highest measured value in these cells was $1.6 \mu\text{m}$, which is less than we estimate to be necessary for good cells. Our collaborators in France have reported (9) values of L_n up to $8 \mu\text{m}$, which is encouraging. The method described in this report should work even better on cells with larger L_n .

Thus several procedures have been developed that should be beneficial for further studies on Cu_2O solar cells.

REFERENCES

1. Metals Handbook, American Society for Metals, 8th edition, 1973. Vol. 8 Metallography, Structures and Phase Diagrams
2. R. A. Logan and A. G. Chynoweth, J. Appl. Phys. 33 1649 (1962)
3. B. L. Smith and M. Abbott, Solid State Electronics 15 361 (1972)
4. A. Baghdadi, et al., Motorola Report No. 2256/11 Oct. 1977-Sept. 1978, Motorola, Inc., 5005 E. McDowell Rd., Phoenix, Ariz, 85008
5. F. L. Weichman, Can. J. Phys. 51 680 (1973)
6. K. E. Hassler, R. E. Heiks and C. L. Meyer, U. S. Patent 2,942,158, June 21, 1960
7. E. D. Tolmie and D. A. Robins, J. Inst. Metals 85 171 (1956)
8. F. Blanie and J. LeHericy, C. R. Acad. Sci., Ser. C 1972 275.
9. C. Noguét, D. Pierrat, M. Tapiéro, and J. P. Zielinger, Revue Phys. Appl. 15 595 (1980)
10. I. M. Kolthoff, P. J. Elving and E. B. Sandell, Treatise on Analytical Chemistry (Interscience, New York, 1962) Part II, Vol. 2, p 169

APPENDIX

(a) Measurements in the nF Range

Considering the circuit in Fig. 11, one can write for the voltage, V_r , across resistance r ,

$$V_r = \frac{V_i r}{R + R_s + r + \frac{R_{sh}}{1 + jC_d \omega R_{sh}}}$$

$$= V_i r \frac{R_{sh} + R + R_s + C_d^2 \omega^2 R_{sh}^2 (R + R_s) + jC_d \omega R_{sh}^2}{(R_{sh} + R + R_s)^2 + C_d^2 \omega^2 R_{sh}^2 (R + R_s)^2}$$

where $r \ll R_{sh} + R + R_s$

If the signal $V_i = V_o \exp(j\omega t)$ is substituted

$$V_r = V_o r \frac{R_{sh} + R + R_s + C_d^2 \omega^2 R_{sh}^2 (R + R_s) \exp(j\omega t)}{(R_{sh} + R + R_s)^2 + C_d^2 \omega^2 R_{sh}^2 (R + R_s)^2}$$

$$+ \frac{V_o r C_d \omega R_{sh}^2 \exp[j(\omega t + \pi/2)]}{(R_{sh} + R + R_s)^2 + C_d^2 \omega^2 R_{sh}^2 (R + R_s)^2}$$

$$R \sim 1000 \gg R_s, \quad r = 10 \, \Omega$$

$$\text{Provided } C_d^2 \omega^2 R_{sh}^2 \ll 1$$

$$V_r = \frac{V_o r}{R_{sh} + R + R_s} \exp(j\omega t) + \frac{V_o r C_d \omega R_{sh}^2 \exp[j(\omega + \frac{\pi}{2})]}{(R_{sh} + R + R_s)^2}$$

$$\text{Thus } V(0) = \frac{V_o r}{R_{sh} + R + R_s}; \quad V(\pi/2) = \frac{V_o r C_d \omega R_{sh}^2}{(R_{sh} + R + R_s)^2}$$

$$\text{and } C_d = \frac{R_{sh} + R + R_s}{\omega R_{sh}^2} \cdot \frac{V(\pi/2)}{V(0)}$$

(b) Measurements in the pF Range

Considering the circuit in Fig. 12 and following similar calculations, one can obtain for the voltage across C, V_C , the following

$$V_C = V_O \frac{R_{sh}^2 R_S R C^2 \omega^2 + R_{sh} (R + R_{sh})}{R^2 R_{sh}^2 C^2 \omega^2 + (R + R_{sh})^2} \exp(j\omega t)$$

$$-V_O \frac{C\omega [R R_{sh}^2 - R_S R_{sh} (R + R_{sh})]}{R^2 R_{sh}^2 C^2 \omega^2 + (R + R_{sh})^2} \exp \left[j(\omega t + \frac{\pi}{2}) \right]$$

For a Au-Cu₂O-Au structure, R_S is due to the gold electrodes and the bulk Cu₂O and is quite small. In this case

$$(R + R_{sh}) R_{sh} R_S \ll R R_{sh}^2$$

and provided $R^2 C^2 \omega^2 \ll 1$, one can write

$$V(0) = \frac{V_O R_{sh}}{R + R_{sh}}; \quad V(\pi/2) = -V_O \frac{C \omega R R_{sh}^2}{(R + R_{sh})^2}$$

and hence
$$C = \frac{R + R_{sh}}{R R_{sh} \omega} \cdot \frac{|V(\pi/2)|}{V(0)}$$

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