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CUPROUS OXIDE PHOTOVOLTAIC CELLS

Final Report for Period September 1, 1978—November 30, 1979

MASTER

By
Dan Trivich

Work Performed Under Contract No. ET-78-S-02-4726

Wayne State University
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U.S. Department of Energy

Solar Energy

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FINAL REPORT

for the period of
September 1, 1978 to November 30, 1979

Contract No. ET-78-S-02-4726

DEPARTMENT OF ENERGY
DIVISION OF ADVANCED ENERGY PROJECTS

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PREFACE

This report covers research done at Wayne State University cuprous oxide photovoltaic cells (solar cells) under Contract No. ER-78-S-02-4995 from the Department of Energy, Division of Advanced Energy Projects during the period of September 1, 1978 to November 30, 1979. Previous work related to this project at Wayne State University is presented in a Final Report on NSF Grant AER-75-23453 (1) and a Final Report on DOE contract No. ET-78-S-02-4726 (2). This previous work has also been reported at ERDA and DOE Program Reviews during 1976-1979 and at IEEE Photovoltaic Specialists Conferences (3,4).

During the period of the present contract, another contract was awarded from the Department of Energy, SERI Photovoltaics Program Office, Emerging Materials Systems for Solar Cell applications, Contract No. DE-AC04-79-ET 23010, with the nominal starting date of April 9, 1979. It was mutually agreed that expenditures from this contract (ET 23010) would begin only after exhaustion of the funds from the Advanced Energy Projects Contract (4995 and the switchover took place early in October, 1979.

In order to make the results of the work promptly available to interested people in the Photovoltaics program, quarterly reports were submitted through Contract No. ET 23010 for the periods of April 9 to July 8, 1979 and July 9 to October 9, 1979. Acknowledgements at the end of these reports made clear that the work was performed under contract No. 4995 from DOE Division of Advanced Energy Projects. The present Final Report covers largely material taken from these two quarterly reports.

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I. INTRODUCTION

Cuprous Oxide (Cu_2O) is of interest as a material for photovoltaic cells because of its low cost, high availability and inexpensive processing. It is a direct band gap semiconductor with a band gap of 2.0 eV which is in the suitable range for solar cells. It has been produced thus far only as a p-type semiconductor so that p-n junctions have not yet been demonstrated. Thus most of the work on Cu_2O cells has been done with Schottky barriers with some explorations of heterojunctions. This has produced cells with a conversion efficiency of 1%.

In the previous work, a variety of Schottky barrier cells with a number of metals as contacts on Cu_2O were studied, and it was found that the measured barrier heights did not show a clear dependence on the work functions of the metals. (1,3) We postulated that this was due to chemical reactions at the Metal/ Cu_2O contacts. This was confirmed, especially for the case of Al/ Cu_2O contacts, by high resolution Auger/ESCA surface studies. (2,4)

The aim of present research was to avoid or prevent this chemical degradation in order to achieve higher barrier heights and thus higher V_{oc} and improved conversion efficiencies. One possible method of preventing this chemical reaction is to interpose a stable oxide interlayer, e.g., Al_2O_3 or SiO_2 , between the metal

and the Cu_2O . Since this layer must be thin in order to allow tunnelling, the structure becomes an MIS structure, which may provide additional advantages.

Another approach to improved Cu_2O solar cells could be through heterojunctions. In favorable cases, i.e., heterojunctions with other oxides, this could avoid the chemical degradation that some Schottky barrier cells display.

Thus the main directions chosen for research on Cu_2O cells in the current phase of the research were the investigation of MIS cells using mainly oxide interlayers and the exploration of heterojunctions on Cu_2O , especially using other oxides.

Other items in the research plan included the preparation of materials including the doping of copper and cuprous oxide; characterization of Cu_2O samples including measurement of optical absorption, diffusion length, resistivity, and Hall effect; exploration of composite cells with lower band gap materials such as silicon; and the development of models for MIS cells, heterojunctions, and Schottky barrier cells.

II. EXPERIMENTAL APPARATUS AND METHODS

Since the new research on MIS and heterojunction cells would require more extensive and versatile equipment for the deposition of oxides and other compounds, the experimental facilities of our laboratory were substantially expanded. In order to maximize the expansion within the budget limitations, the equipment was largely assembled from purchased or laboratory-built components and fixtures.

A. Ion Sputtering Apparatus

The ion sputtering system was built around a 2.5 cm Ion Tech ion source, using a Varian 6 in oil-pumped vacuum system as a base. The ion gun base plate is mounted on an 18" diameter glass cylinder vacuum chamber. Suitable power supplies have been built or purchased. A plasma bridge neutralizer has been added. A sample holder was constructed and provided with facilities for heating and cooling of samples, application of bias, and measurement of I-V characteristics in the vacuum system. The sputtering targets can be mounted on a four-position carousel holder. A pan type holder allows the use of powders in the target. In addition, metal coating can be done from a shielded resistance-heated source.

This equipment has been used to sputter a variety of materials in argon or oxygen, such as SiO_2 , Al_2O_3 , CdO , ZnO , Al , In_2O_3 , etc.

B. Electron Beam Evaporation Apparatus

The electron beam equipment was installed in a Perkin-Elmer Ultek ultrahigh vacuum system, Automatic Rapid Cycle A-RCS, with an 18" x 30" bell jar. This is a non-oil system and uses an ion pump together with a Cryopump CFR. The E-gun which was installed in this apparatus is an Airco-Temescal 4-pocket turret, Model STIH-270-1. This is powered by a Sloan electron beam power supply of 5 KW and 10 KV, equipped with an X-Y sweep. Appropriate sample holders and a crystal deposition monitor have been installed. A separate resistance-heated source has also been provided.

C. Apparatus for Evaluation of MIS Structures.

The apparatus for measuring cell parameters has also been upgraded and expanded. Two separate sets of equipment have been assembled to measure I-V and capacitance-voltage (C-V) curves. One of the sample holders is shielded and temperature-controlled, so that measurements can be made from 15° C to 90° C. Modifications are being made on the other sample holder to give it similar capabilities. The power supply has been modified to allow it to be bipolar without switching and also to absorb up to 200 mA of current from a photocell without affecting its accuracy. Figure 1 is a block diagram of the experimental setup. The current output of the cell is measured by measuring the voltage drop across a standard resistor in series with the cell. The capacitance is measured by superimposing a small AC voltage on the DC bias voltage. The AC signal developed across the measurement resistor is measured with a PAR Model 124 lock-in amplifier.

The spectral response curves on the cells are measured with essentially the same equipment that has been used for the surface photovoltage measurements. Figure 2 shows a block diagram for this apparatus. The monochromator is a SPEX Model 1704 Spectrometer and has a spectral band pass of 5 Å or less for the slit setting of 0.5 mm or less used in these experiments. For spectral response measurements the photovoltaic cell is placed in the sample holder with the top contact fingers directly contacting a tin oxide coated transparent electrode, whereas for the SPV measurements a transparent dielectric is placed between the top surface of the Cu_2O sample and the top transparent electrode.

Figure 1. Experimental Setup for IV and C-V Measurements on Solar Cells

Figure 2. Experimental Setup for Spectral Response and Surface Photovoltage Measurements

III. ELECTRONIC PROPERTIES OF MIS STRUCTURES.

A. Preparation and Photovoltaic Characteristics

A number of MIS structures were prepared on Cu_2O using various metals as top contacts and several oxides as interlayers. The oxides SiO_2 and Al_2O_3 were examined first in order to select the best candidate for MIS cells. Films of these oxides were deposited on Cu_2O by ion sputtering in the apparatus described above, and the structures were examined by depth profiling using high resolution Auger/ESCA techniques. The $\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$ structure showed as much as 20% Cu(O) at the interface indicating the presence of the chemical reaction previously postulated, presumably in this case due to some residual reducing action in the AlO_x as deposited. The $\text{SiO}_2/\text{Cu}_2\text{O}$ appeared to be relatively free of Cu(O) but a faint trace may have been present. Thus the SiO_2 deposit was chosen as the best producible by present techniques for use as an interlayer.

A number of MIS cells were prepared on Cu_2O using SiO_2 as the interlayer and using gold, silver, copper and aluminum as top contacts. The thickness of the SiO_2 was varied from 10 Å to 150 Å and greater. Table I shows the types of cells that were prepared and gives the photovoltaic properties. As the table shows, the cell resistance increased with increasing thickness of oxide, and above 100 Å, there was a marked increase. Since tunneling through a smooth uniform interlayer should be effective only below 40 Å, this indicates that the SiO_2 interlayers are non-uniform in thickness, or they contain partial shorts or inclusions of conductive material, or that some conductivity mechanism other than tunnelling is present. Another

TABLE I. Photovoltaic Properties of Cuprous Oxide MIS Cells.

Top Contact	SiO ₂ Thickness Å	Cu ₂ O Resistivity Ω·cm	J _{sc} mA/cm ²	V _{oc} V	Cell Resistance Ω
Gold	10	95	Ohmic Junction		5
	20	200	No Photoresponse		12
	40	480			91
	60	340			96
	80	780			440
	100	890			230
Silver	10	250	0.75	0.055	30
	20	250	0.25	0.025	33
	40	170	0.04	0.025	45
	100	220	0.005	0.004	350
Copper	10	95	1.35	0.08	20
	20	200	0.10	0.04	65
	40	480	0.20	0.03	50
	60	340	0.15	0.08	60
	80	780	Slight Photores.		130
	100	890	Slight Photores.		220
Aluminum	10	250	1.4	0.24	35
	20	200	1.25	0.25	45
	40	170	0.15	0.11	45
	60	250	0.10	0.19	150
	100	220	0.03	0.14	190
	150	250	No Photoresp.		2500
	500	220	No Photoresp.		12,000

result shown in the table is that the V_{OC} increased from Au to Ag to Cu to Al, which is the order of decreasing work function of these metals. Gold, as we had established previously, gave an ohmic contact in these MIS structures, as it does with Au/Cu₂O "Schottky type" junctions. The silver MIS cells also gave the type of performance expected from the corresponding Schottky barrier cell. However, the results for the Cu MIS cells were poorer than expected from a comparison with Schottky cells. This may indicate some difficulty in making good junctions in these MIS cells rather than a degradation due to the insertion of the SiO₂ layer. The aluminum MIS cells were the best of the series but still not up to the performance of the usual Al/Cu₂O cell.

B. Current-Voltage Characteristics

The dark I-V characteristics of these MIS cells are shown as semilogarithmic plots in Figures 3, 4, and 5. Assuming the applicability of the equation

$$J = J_0 [\exp(qV/nkT) - 1]$$

the values of the ideality factor n and the values of J_0 were obtained. Applying the Richardson equation to J_0 , the values of the barrier heights were calculated. The values for n and ϕ_B are shown on the corresponding figures.

The barrier heights for the silver and the copper MIS cells are very similar to each other but somewhat lower than the 0.68 eV normally obtained for a Cu/Cu₂O cell. The barrier heights for the two thinner aluminum MIS cells are similar to that for a Cu/Cu₂O cell. These cells may in fact be Cu/Cu₂O Schottky barriers,

Figure 3. Dark J-V Curves for Ag/SiO₂/Cu₂O MIS Cells of Various Oxide Thicknesses

Figure 4. Dark J-V Curves for Cu/SiO₂/Cu₂O MIS Cells of Various Oxide Thicknesses

Figure 5. Dark J-V Curves for Al/SiO₂/Cu₂O MIS Cells of Various Oxide Thicknesses

arising from a chemical reaction of the aluminum with the Cu_2O through pores in the SiO_2 layers.

The semilogarithmic I-V curves for the thicker aluminum MIS cells do not yield linear plots and the extrapolated values of J_0 give considerably higher calculated values of the barrier height. These could be examples of MIS structures in which the n-value varies with applied voltage in a manner similar to the theoretical model of Card and Rhoderick. (5)

C. Spectral Response of the MIS Cells.

The spectral response of a number of the MIS cells was measured. Figure 6 shows the spectral response for a set of $\text{Cu/SiO}_2/\text{Cu}_2\text{O}$ cells of different thicknesses of SiO_2 . Similar results were obtained for the other cells. The peak at 2.6 eV may correspond to a peak in the absorption spectrum as given by Pastrnak (6). However, in some preliminary measurements in our laboratory, we have not confirmed the existence of this peak in the absorption spectrum. While our results agree with Pastrnak's at lower frequencies, the values of the absorption at the expected peak ($\sim 10^4 \text{ cm}^{-1}$) gave too small a light transmission to measure in the spectrophotometer. We are attempting to prepare thinner samples in order to measure the absorption coefficient in this region.

D. Junction Capacitance Measurements

Since the capacitance of MIS structures can be used to determine some features of the junction and its depletion layer as well as the insulating layer, a series of capacitance measurements were made on

Figure 6. Spectral Response of Cu/SiO₂/Cu₂O MIS Solar Cells

the MIS cells prepared for the I-V and spectral response measurements. The apparatus and methods used were described in an earlier section. Some preliminary results are presented here.

The results can sometimes be represented by linear plots of $1/C^2$ vs V . Figures 7 and 8 show the data for Al/SiO₂/Cu₂O and Ag/SiO₂/Cu₂O MIS structures with different thicknesses of SiO₂. The intercepts for the aluminum MIS cells with 10 and 20 Å SiO₂ are about 0.35 to 0.4 V which are similar to those for the Al/Cu₂O Schottky barrier cells. However, for the Al MIS cell with 40 Å SiO₂, the intercept is 1.2 V, which does not appear to be reasonable for the built-in potential for this system. For thick SiO₂ layers, the capacitive reactance of the insulating layer becomes appreciable.

The majority carrier concentrations for the 10 Å and 20 Å SiO₂ cells are about 10^{15} cm^{-3} , and the depletion width is 1 μm, which is larger than we had previously assumed.

The junction capacitance of the silver MIS structures was too small to measure accurately in the presence of the large diode leakage currents. Therefore, the data shown for the Ag/SiO₂Cu₂O cells are of a very preliminary nature but they show the same trends in voltage and frequency dependence as those of the aluminum cells.

In the case of the gold MIS structures, it was not possible to measure a depletion layer capacitance. The measured capacitance was independent of voltage and presumably was due to the SiO₂ insulating layer. In the case of gold contacts on Cu₂O, which are ohmic, there is no band bending and no depletion layer.

Figures 9 and 10 show the frequency dependence of the capacitance for aluminum and gold MIS structures. The rapid rise of

Figure 7. Plots of $1/C^2$ vs. Applied DC Bias for Al/SiO₂/Cu₂O MIS Cells of Various Oxide Thicknesses

Figure 8. Plots of $1/C^2$ vs. Applied DC Bias for Ag/SiO₂/Cu₂O MIS Cells of Various Oxide Thicknesses

Figure 9. Frequency Dependence of the Junction Capacitance of an Al/SiO₂/Cu₂O MIS Cell

Figure 10. Frequency Dependence of the Junction Capacitance of an Au/SiO₂/Cu₂O MIS Cell

capacitance with decreasing frequency may be due to the presence of slow traps, possibly both in the insulating layer and at the $\text{SiO}_2/\text{Cu}_2\text{O}$ interface. Future studies of the temperature dependence of the capacitance may help to identify the nature of these traps.

E. Discussion of MIS Properties

For the metals studied, the MIS cells gave increased values of V_{oc} and barrier height in the order of decreasing work function of the metal, i.e., gold, silver, copper and aluminum. Thus it appears that in these cells, the work function of the metal plays a dominant role in determining the degree of band bending and V_{oc} , and that interface states play a secondary role. The results of the capacitance measurements are also consistent with the view that there is no band bending with Au in MIS cells, some with Ag and more with Cu and Al. However, there is an indication that some deep traps are present.

IV. HETEROJUNCTIONS ON Cu_2O

In order to avoid the chemical degradation observed in some Cu_2O Schottky barrier cells, two approaches were proposed. One was to interpose an oxide interlayer between the metal and the Cu_2O . This gives MIS structures and these were discussed in the previous section. The other approach was to use heterojunctions with other oxides. This section presents some results obtained for heterojunctions on Cu_2O with SnO_2 , In_2O_3 , CdO and mixtures of CdO and SnO_2 .

A. General Procedures for the Study of Heterojunctions

The Cu_2O samples were prepared as previously described (3) by thermal oxidation of copper sheet, followed by annealing, polishing and etching in 8M HNO_3 solution. Both polycrystalline and grain growth (7) single crystal samples were used.

The other semiconductor oxides were applied by ion sputtering using the apparatus described in the previous sections. The oxide targets consisted of pure commercial powders contained in a tray type holder. The atmosphere used was argon. The deposition thickness was measured with a quartz crystal monitor. Some of the oxide films were also deposited on glass to allow measurement of the resistivity and optical absorption of the films. The I-V characteristics of the $\text{MO}_x/\text{Cu}_2\text{O}$ heterojunction cells were measured in the dark and under illumination. Representative cells were subjected to Auger analysis. This served to verify the nominal composition of the coating and to check for the possible contamination by tungsten from the filament. More importantly, a number of the cells showed the presence of Cu(O) at the interface indicating chemical deterioration, i.e. reduction to form a $\text{Cu/Cu}_2\text{O}$ junction. This effect appeared to correlate with a higher series resistance in the cell, so that this property was sometimes used to infer the presence of the chemical reaction. One type of heterojunction cell, $\text{CdO/Cu}_2\text{O}$, prepared at room temperature showed no presence of Cu(O) at the interface, so that a true oxide heterojunction can be assumed to exist in this case. This type of cell was examined in detail.

B. $\text{SnO}_2/\text{Cu}_2\text{O}$ Heterojunction Cells

The $\text{SnO}_2/\text{Cu}_2\text{O}$ junction was prepared at room temperature by sputtering from a SnO_2 powder source. The thickness of the SnO_2 film

was 750 Å. The I-V curves for a junction of this type are shown in Fig. 11. An Auger spectrum of this junction was not taken but the high series resistance is an indication that the junction is not a good one. This indicates that some chemical degradation may have occurred at the interface. However, the SnO₂ coating appears to have some value as an anti-reflection coating. Also its greater chemical stability against atmospheric attack can be used to protect the CdO/Cu₂O junction, as described later.

C. In₂O₃/Cu₂O Heterojunction Cells

Several substrate temperatures were used to prepare the In₂O₃/Cu₂O junction. The junction prepared at room temperature had a low series resistance but the other cells prepared at higher temperatures had high series resistance. This was the first indication of chemical reactions at the interface which could be correlated with the development of high cell series resistance. The I-V characteristics of some typical In₂O₃/Cu₂O junctions are shown in Fig. 12. Fig. 12a is for a cell prepared at room temperature and Fig. 12b is for a cell prepared at 150°C.

Auger analyses were made of some In₂O₃/Cu₂O junctions in order to check the possibility of chemical reactions at the interface. Fig. 13 shows an AES spectrum of the top surface of an In₂O₃/Cu₂O cell formed at 150°C. The most prominent features are of In and O. There is no indication of any Cu(O) at the surface. There are traces of S and C, which are frequently found for surfaces exposed to the atmosphere, but no tungsten was found. In general, no tungsten contaminant was found in any of the cells examined.

Figure 11. Current-Voltage Characteristics of a SnO₂/Cu₂O Heterojunction Cell

Figure 12. Current-Voltage Characteristics of an $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ Heterojunction Cell

MOD= 3
3.00KV, .800UA
FILE: INSVR

SF= 7.172
DAT= 4.33
ROOM TEMP

09/17/79

Figure 13. Auger Spectrum of the Top Surface of an $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ cell

The AES depth profile of this junction obtained by successive high resolution scans is shown in Fig. 14. High resolution scans of the MVV Auger peak for this junction are shown in Fig. 15. These show the presence of the Cu(O) at the interface which therefore supports the hypothesis of a chemical reaction at the interface.

The analogous depth profile and high resolution scans of the Cu MVV Auger peak of an $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ junction prepared at room temperature are shown in Figs. 16 and 17 respectively. These also show the presence of Cu(O) at the interface but considerably less than for the 150°C sample. This indicates that the use of higher substrate temperature leads to a greater degree of chemical degradation at the junction.

D. CdO/ Cu_2O Heterojunction Cells

1. General - The CdO/ Cu_2O heterojunction system was studied in greater detail since, in exploratory studies, it showed the best possibilities for avoiding the chemical reactions at the interface. In addition to the heterojunction cells, thin CdO films on glass were prepared for study. The sputtering was done in an argon atmosphere using CdO powder. Different substrate temperatures were used, from room temperature to 200°C , and the thickness of the CdO films was varied.
2. Properties of CdO Films - The properties of the CdO films did not change greatly over the range of conditions studied, e.g. from room temperature to 200°C for the substrate. The optical absorption varied with the film thickness, of course, and the calculated resistivity also depended somewhat on thickness. Fig. 18 shows the optical transmission of CdO films of thicknesses $650 \text{ \AA}$, $1000 \text{ \AA}$, and $1500 \text{ \AA}$. The resistivities were 9.5×10^4 , and 3.7×10^4 , and $2.2 \times 10^4 \Omega \cdot \text{cm}$, respectively. These data indicate that the optimum thickness of CdO is about $1000 \text{ \AA}$. Although the resistivity of the CdO films on glass

Figure 14. Auger Depth Profile of an $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ Heterojunction Cell Prepared at 150°C.

Cu MVV cycles 10, 12, ... 22

Figure 15. High Resolution Scans of the Cu MVV Auger Peak
in an In_2O_3 Junction Made at 150°C.

Figure 16. Auger Depth Profile of an $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ Heterojunction Cell Prepared at Room Temperature.

cycles 5, 7, 9, 11, 13, 15

Figure 17. High Resolution Scans of the Cu MVV Auger Peak
in an $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ Junction Prepared at Room Temperature

Figure 18. Optical Transmission of CdO Films of Various Thicknesses

was quite high, the CdO films on Cu₂O appeared to be satisfactorily conductive, especially with Al fingers as contacts.

3. CdO/Cu₂O Cells prepared at 200°C - The I-V characteristics of a CdO/Cu₂O cell prepared at 200°C are shown in Fig. 19. The series resistance of this cell is high. Auger analyses of cells of this type show some reduction to Cu(O) at the interface. Fig. 20 shows that the surface consists predominantly of Cd and O, with the usual presence of S and C from the atmosphere. Fig. 21 shows an AES depth profile of the junction. Apart from the expected transition from CdO to Cu₂O, the significant result in this diagram is the presence of small but definite amounts of Cu metal, Cu(O), beginning at the interface. Fig. 22 shows a high resolution scan of the Cu MVV peak, and this also shows that traces of Cu(O) are present. While the amount of Cu(O) found is not large, the evidence for some reduction is quite definite.

4. CdO/Cu₂O Cells Prepared at Room Temperature - The results on the CdO/Cu₂O heterojunctions prepared at room temperature were quite encouraging. The Cu₂O samples were etched in 8M HNO₃ for 10-15 seconds and, after washing and drying, were placed in the vacuum system as soon as possible. The Cu₂O substrate was heated to 110°C for a few minutes and then brought back to room temperature. This heat treatment could be replaced by an argon ion beam etch with similar results. The CdO film was then applied by argon ion beam sputtering from a CdO powder source.

Figure 23 shows the I-V characteristics of a CdO/Cu₂O heterojunction cell prepared at room temperature. The V_{oc} of cells of this type was always about 0.3 V and the best value was 0.4 V. The J_{sc} was between 1 and 2 mA/cm². The cell series resistance was quite low e.g. 10-35 Ω for cells prepared from Cu₂O of resistivities of ~150 Ω·cm.

Figure 19. Current-Voltage Characteristics of a CdO/Cu₂O Cell Prepared at 200°C

Figure 20. Auger Spectrum of the Surface of a CdO/Cu₂O Cell.

Figure 21. Auger Depth Profile of a CdO/ Cu₂O Cell Prepared at 200°C.

Figure 22. High Resolution Scans of the Auger Cu MVV Peak
in a CdO/ Cu₂O Junction Prepared at 200°C.

Figure 23. Current-Voltage Characteristics of a CdO/Cu₂O Heterojunction Cell

Prepared at Room Temperature

The Auger spectrum of the surface of a CdO/Cu₂O cell is shown in Fig. 24. The depth profile is shown in Fig. 25 and the high resolution scans are shown in Fig. 26 and Fig. 27. The high resolution scans and the depth profile show no evidence of any Cu(O) at the interface. This indicates that the junction is a true heterojunction between CdO and Cu₂O and shows that it is possible to prepare heterojunctions between Cu₂O and other semiconductor oxides by the development of the suitable conditions of preparation.

5. Detailed Analysis of Current-Voltage Characteristics - The CdO/Cu₂O heterojunction cells prepared at room temperature were subjected to a detailed study of I-V characteristics at various temperatures. In the results quoted below the resistivity of the Cu₂O was 150 $\Omega \cdot \text{cm}$ and the cell resistance was 10 Ω at room temperature. The I-V characteristics were measured from 296 K to 346 K. The results could be fitted to the equation

$$J = J_0 \exp [C(V - JR_s)]$$

Fig. 28 shows the plots of $\ln J$ vs. $(V - JR_s)$ at the various temperatures. The plots are linear and yield the experimental values of J_0 and C , which are listed in Table II. The table also gives the value of n calculated from $C = 1/(nkT)$. The results are characterized by rather high values of J_0 and n .

6. Heterojunctions with Sn-doped CdO - Films of CdO containing SnO₂ were made by sputtering on Cu₂O. The sources were CdO powder containing 8 or 14 mole percent SnO₂ in powder form. Cells were obtained with V_{oc} up to 0.35 V and J_{sc} of 2 to 2.2 mA/cm², but with high cell resistances. However, Auger analysis showed the presence of considerable amounts of Cu(O) at the interface. From a comparison with the CdO/Cu₂O cells, it is possible to conclude that Sn is the element that leads to the chemical reduction of the Cu₂O.

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Figure 24. Auger Spectrum of the Surface of a CdO/Cu₂O Cell Made at Room Temperature

Figure 25 Auger Depth Profile of a CdO/Cu₂O Cell prepared at Room Temperature

Figure 26. High Resolution Scans of the Auger Cu MVV Peak
in a CdO/Cu₂O Junction Prepared at Room Temperature

Figure 27. High Resolution Scans of the Auger Cu MVV Peak
in a CdO/Cu₂O Junction Prepared at Room Temperature

Figure 28. Plots of $\ln J$ vs. $V - JR_s$ for a $\text{CdO/Cu}_2\text{O}$ Cell at Various Temperatures

TABLE II

I-V PARAMETERS FOR A CdO/Cu₂O HETEROJUNCTION

TEMP. (°K)	J_0 (A/cm ²)	C (V ⁻¹)	n
296	1.4×10^{-4}	7.2	5.55
308	1.9×10^{-4}	7.4	5.03
317	2.5×10^{-4}	7.3	5.02
326	2.8×10^{-4}	7.6	4.73
338	3.6×10^{-4}	7.8	4.86
346	3.9×10^{-4}	8.5	4.35
298**	1.5×10^{-4}	7.8	5.00

** After cooling to room temperature

7. Stability of the CdO/Cu₂O Heterojunction Cells - The CdO/Cu₂O

cells were checked for stability in air over the period of days. After standing 10 days, the cell suffered a degradation of 0.1 V in V_{oc} , but changed very little in J_{sc} and cell resistance. Beyond 10 days standing, the characteristics changed rapidly in that V_{oc} and J_{sc} decreased and R_s increased.

We surmised that the degradation of the cell was due to atmospheric attack on the CdO, from the outside rather than chemical reactions at the interface, since it is known that CdO will react with water and CO₂. An attempt to protect the cell with a top coating of SnO₂ was tried since SnO₂ is more stable against atmospheric attack. A SnO₂/CdO/Cu₂O structure was prepared by sputtering a 500 Å film of CdO followed by a 300 Å film of SnO₂ on the CdO. This structure proved to be more stable than the CdO/Cu₂O cells previously examined. In 10 days, the V_{oc} decreased by only 0.03 V, the J_{sc} remained constant and R_s showed a small decrease.

E. Summary and Discussion of Heterojunction Results

Table III lists the oxide heterojunction systems that were studied and gives the best values of V_{oc} and J_{sc} obtained for these cells as a function of the substrate temperature. Also the evidence for chemical reduction to Cu(O) at the interface is given. The heterojunction cell of CdO/Cu₂O prepared at room temperature did not show any reduction to Cu(O) at the interface.

While it is not yet established whether these photovoltaic characteristics arise from Cu/Cu₂O junctions or oxide heterojunctions, the contacts of Cu₂O with SnO₂ or In₂O₃ might, in any case, yield low values for V_{oc} in view of the relatively high electron affinities of

these materials, i.e. 4.8 V for SnO_2 and 4.45 eV for In_2O_3 . The electron affinity of CdO is not known but the higher V_{oc} implies that it may be closer to that for Cu_2O , 3.27 eV.

The results with the CdO/ Cu_2O cells are important because they show that the chemical reduction to Cu(O) at the interface can be avoided and that true heterojunctions of semiconductor oxides on Cu_2O can be prepared with suitable choice of conditions. The cell is stable over short periods of time so that reproducible measurements can be made over reasonable periods of time; the cell degrades but this appears to be due to atmospheric attack rather than reactions at the heterojunction interface. The cell can be protected to some extent by an overlayer of SnO_2 on top of the CdO. It may be possible to further stabilize the cell with other coatings or encapsulants. However, the chief importance of the CdO/ Cu_2O cell is that it establishes, in principle, that successful heterojunctions can be prepared with other oxide semiconductors. Therefore the study can be expanded to a number of other oxides with some optimism.

It has been established that the conditions of deposition by ion sputtering are quite important in obtaining good cells. It is advisable therefore to explore further variations in conditions. In particular, it is planned to use mixtures of oxygen with argon in order to improve the stoichiometry of the oxides and thus prevent the reduction of the Cu_2O .

The quality of the CdO/ Cu_2O junction could perhaps be further improved. The high values of J_0 and n indicate an imperfect junction. It is possible that the properties are poor due to multiple step tunnelling mechanism at the junction. This may be due to defects and dislocations in the Cu_2O . High dislocation densities have been observed in grain growth Cu_2O (8). Suitable annealing procedures have been shown (9) to improve the quality of cuprous oxide single crystals.

TABLE III

CHARACTERISTICS OF OXIDE HETEROJUNCTIONS WITH Cu_2O

X / Cu_2O	Subs. Temp. ($^{\circ}\text{C}$)	V_{oc} (mV)	J_{sc} (mA/cm^2)	Chemical Reaction
SnO_2	room temp.	230	1.5	Suspectible
	—	—	—	—
In_2O_3	room temp.	250	2.0	Very small
	150	300	2.0	Considerable
CdO	room temp.	400	2.0	None
	200	280	1.0	Very small
$\text{CdO}(\text{SnO}_2)$	room temp.	280	1.7	Considerable
	200	360	2.2	Large
SnO_2/CdO	room temp.	210	1.5	None
	—	—	—	—

V. SUMMARY AND CONCLUSIONS

The research described in this report represents the beginning of a second phase of research on cuprous oxide photovoltaic cells. The first phase was concerned with the development of procedures of making Schottky barriers on isolated films of Cu_2O , including single crystals. It was found that properties of these Schottky barrier cells, in particular the barrier heights, were limited by chemical changes at the junction especially with metals of low work function which tend to be more active chemically, e.g. Al.

The motivation of the present phase of the research was to construct junctions that would avoid this chemical degradation while maintaining electrical contact between the Cu_2O and a low work function material in order to attain larger barrier heights. Essentially the approach involved placing the Cu_2O in contact with a stable oxide. When this oxide is used as a thin layer between the Cu_2O and a top metal contact this gives an MIS structure. As another approach the other oxide can be an n-type semiconductor in thicker layers to form a heterojunction.

Apparatus was constructed to deposit the oxide layers, especially by ion sputtering. It proved to be important to examine the junctions by the detailed surface analysis techniques of Auger analysis, using high resolution in order to differentiate between Cu(I) and Cu(0). It was found that sputtered films of several oxides including aluminum oxide gave Cu(0) at the junction. This was surprising because one would expect aluminum oxide to be relatively stable. Silicon dioxide proved to give the most stable junctions.

The series of MIS cells made with SiO_2 interlayers and top contacts of Au, Ag, Cu, and Al showed a gradation in photovoltaic properties, in the order expected from the work functions of the metals. Thus it can be concluded that the work function of the metal is dominant in establishing the barrier height and that the Fermi level is not pinned by surface states. This offers the hope that eventually higher barrier heights can be achieved by using lower work function metals when the effective chemical barrier is achieved.

In the case of the heterojunctions with other oxides, again the Auger technique under high resolution was valuable in establishing the cases in which chemical reduction occurred at the junction, as summarized in Table III. It was shown that the chemical reduction did not occur in the case of the $\text{CdO}/\text{Cu}_2\text{O}$ heterojunction prepared at room temperature. This established that a true heterojunction cell can be prepared with Cu_2O , provided that one uses the proper conditions.

At this point, the research on oxide layers on Cu_2O has been largely exploratory but has succeeded in establishing several important points. It was shown that the deposition of some of the oxides caused reduction of the Cu_2O to Cu(O) under certain conditions. It may be possible to avoid this chemical degradation by using lower substrate temperatures, or other variations in deposition conditions. Another possibility is that the oxides are non-stoichiometric, even though one would have expected aluminum oxide to be more stable than cadmium oxide. Another change in deposition conditions that is planned is to use mixtures of oxygen and argon in the inlet gas

for ion sputtering in hopes of improving the stoichiometry of the deposited oxides.

The problem of depositing effective thin layers of oxides as an interlayer in MIS cells may be difficult because in layers of $20\text{\AA}$ thickness it may not be possible to achieve uniform films without pinholes through which the metal could contact the Cu_2O . Nevertheless some further research in this area is justified.

It is easier to be optimistic about heterojunctions on Cu_2O in view of the promising results with the $\text{CdO}/\text{Cu}_2\text{O}$ cells. Therefore it is planned to emphasize this approach to making junctions in Cu_2O with greater attention to the details of the deposition process and with some attempt to control stoichiometry. This will be done especially with n-type oxides of low work function and low electron affinity.

While there are a number of other aspects of research on Cu_2O photovoltaic cells which will require attention, the most important problem is to increase the barrier height and thus the V_{oc} . The research described in this report has shown some promising approaches to reaching this goal.

PERSONNEL

Professor E. Y. Wang of the Department of Electrical and Computer Engineering was a co-principal investigator during much of this project. Since August, 1979, he has been a visiting professor at Arizona State University in Tempe, and he has continued as a consultant on this project.

Dr. Richard J. Komp was a Senior Research Associate on the project. Other research associates that were associated with the work are Dr. Tzer-Fe Huang, Mr. Leonidas Papadimitriou and Dr. Ali Bazzi. Dr. Ali Rakhshani has recently joined the group. Mr. David Brinker, Mr. George Thomas and Mr. Dennis Fish are graduate students who have participated in some of the research.

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