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CUPROUS OXIDE PHOTOVOLTAIC CELLS

Second Quarterly Technical Progress Report for July 9–October 8, 1979

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MASTER

U.S. Department of Energy

Solar Energy

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CUPROUS OXIDE PHOTOVOLTAIC CELLS

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for the Period of July 9, 1979, to October 8, 1979

to the Department of Energy
SERI Photovoltaics Program Office
Emerging Materials Systems for Solar Cell Applications

Contract No. DE-AC04-79-ET23010

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I. INTRODUCTION

Much of the previous work on cuprous oxide (Cu_2O) solar cells was done on Schottky barriers, e.g. $\text{Cu}/\text{Cu}_2\text{O}$ junctions. When other metals were used on Cu_2O , especially metals with lower work functions, it was found that the V_{oc} did not improve significantly and that the barrier height did not change appreciably (1). An explanation proposed for these results is that the metals of lower work function are usually more active chemically and they reduce the surface of the Cu_2O , so that the junctions change to $\text{Cu}/\text{Cu}_2\text{O}$ junctions as a result of the chemical reaction. This hypothesis was supported (2) by direct high resolution Auger analysis of the interface which confirmed the presence of copper metal, $\text{Cu}(0)$, at the interface.

Two methods have been proposed to avoid this chemical degradation. One is to interpose a thin impervious oxide layer between the Cu_2O and the metal. This yields an MIS structure. A study of some MIS cells of this type was presented in the previous quarterly report (3). Some of the oxide interlayers, as prepared, also proved not to be completely stable. However, SiO_2 interlayers proved to yield the most stable MIS cells, so that these were selected for more detailed study, especially by capacitance measurements (3).

The other proposed approach is to use heterojunctions with other, suitably selected oxide semiconductors. This report presents some of the work done so far on heterojunctions of Cu_2O with SnO_2 , In_2O_3 , CdO and mixtures of CdO and SnO_2 .

II. GENERAL PROCEDURES

The Cu_2O samples were prepared as previously described (1) by thermal oxidation of copper sheet, followed by annealing, polishing and etching in

8M HNO_3 solution. Both polycrystalline and grain growth (4) single crystal samples were used (7).

The other semiconductor oxides were applied by ion sputtering using the apparatus described in the previous quarterly report. 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 $\text{Cu}(0)$ at the interface indicating chemical deterioration, i.e. reduction to form a $\text{Cu}/\text{Cu}_2\text{O}$ 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, $\text{CdO}/\text{Cu}_2\text{O}$, prepared at room temperature showed no presence of $\text{Cu}(0)$ 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.

III. INVESTIGATION OF OXIDE HETEROJUNCTIONS

A. $\text{SnO}_2/\text{Cu}_2\text{O}$ 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 $750 \text{ \AA}$. The I-V curves for a junction of this type are shown in Fig.1. An Auger spectrum of this junction was not taken but the high series resistance is an indication that the

Figure 1. Current-Voltage Characteristics of a SnO₂/Cu₂O Heterojunction Cell

junction is not a good one. This indicates that some chemical degradation may have occurred at the interface. However, the SnO_2 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 $\text{CdO}/\text{Cu}_2\text{O}$ junction, as described later.

B. $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ Heterojunction Cells

Several substrate temperatures were used to prepare the $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ 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 $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ junctions are shown in Fig. 2. Fig. 2a is for a cell prepared at room temperature and Fig. 2b is for a cell prepared at 150°C .

Auger analyses were made of some $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ junctions in order to check the possibility of chemical reactions at the interface. Fig. 3 shows an AES spectrum of the top surface of an $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ cell formed at 150°C . The most prominent features are of In and O. There is no indication of any Cu(0) 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.

The AES depth profile of this junction obtained by successive high resolution scans is shown in Fig. 4. High resolution scans of the MVV Auger peak for this junction are shown in Fig. 5. These show the presence of Cu(0) at the interface which therefore supports the hypothesis of a chemical reaction at the interface (8).

Figure 2. Current-Voltage Characteristics of an $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ Heterojunction Cell

3.00KV, .800UA
FILE: INSR

DRT = 4.33
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Figure 3. Auger Spectrum of the Top Surface of an $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ cell

Figure 4. 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 5. High Resolution Scans of the Cu MVV Auger Peak
in an In_2O_3 Junction Made at 150°C.

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. 6 and 7, respectively. These also show the presence of Cu(0) 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.

C. $\text{CdO}/\text{Cu}_2\text{O}$ Heterojunction Cells

1. General — The $\text{CdO}/\text{Cu}_2\text{O}$ 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. 8 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 , 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 was quite high, the CdO films on Cu_2O appeared to be satisfactorily conductive, especially with Al fingers as contacts.
3. $\text{CdO}/\text{Cu}_2\text{O}$ Cells Prepared at 200°C — The I-V characteristics of a $\text{CdO}/\text{Cu}_2\text{O}$ cell prepared at 200°C is shown in Fig. 9. The series resistance of this cell

Figure 6. 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 7. 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 8. Optical Transmission of CdO Films of Various Thicknesses

Figure 9. Current-Voltage Characteristics of a CdO/Cu₂O Cell Prepared at 200°C

is high. Auger analyses of cells of this type show some reduction to Cu(0) at the interface. Fig. 10 shows that the surface consists predominantly of Cd and O, with the usual presence of S and C from the atmosphere. Fig. 11 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(0), beginning at the interface. Fig. 12 shows a high resolution scan of the Cu MVV peak, and this also shows that traces of Cu(0) are present. While the amount of Cu(0) 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 13 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 $\sim 150 \Omega \cdot \text{cm}$.

The Auger spectrum of the surface of a CdO/Cu₂O cell is shown in Fig. 14. The depth profile is shown in Fig. 15 and the high resolution scans are shown in Fig. 16 and Fig. 17. The high resolution scans and the depth profile show no evidence of any Cu(0) at the interface. This indicates that the junction is a

Figure 10 Auger Spectrum of the Surface of a CdO/Cu₂O Cell.

Figure 1. Auger Depth Profile of a CdO/ Cu₂O Cell Prepared at 200°C.

Figure 12. High Resolution Scans of the Auger Cu MVV Peak
in a CdO/ Cu₂O Junction Prepared at 200°C.

Figure 13 Current-Voltage Characteristics of a $\text{CdO/Cu}_2\text{O}$ Heterojunction Cell

Prepared at Room Temperature

Figure 14. Auger Spectrum of the Surface of a CdO/Cu₂O Cell Made at Room Temperature

Figure 15 Auger Depth Profile of a CdO/Cu₂O Cell prepared at Room Temperature

Figure 16. High Resolution Scans of the Auger Cu MVV Peak
in a CdO/Cu₂O Junction Prepared at Room Temperature

Figure 17. High Resolution Scans of the Auger Cu MVV Peak
in a CdO/Cu₂O Junction Prepared at Room Temperature

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 Ω·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. 18 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 I. 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(0) 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.

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

Figure 18. Plots of $\ln J$ vs. $V - JR_s$ for a $\text{CdO/Cu}_2\text{O}$ Cell at Various Temperatures

TABLE I

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
325	2.8×10^{-4}	7.6	4.73
338	3.6×10^{-4}	7.8	4.86
345	3.9×10^{-4}	8.5	4.35
298**	1.5×10^{-4}	7.8	5.00

** After cooling to room temperature

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 CO_2 . An attempt to protect the cell with a top coating of SnO_2 was tried since SnO_2 is more stable against atmospheric attack. A $SnO_2/CdO/Cu_2O$ structure was prepared by sputtering a 500 Å film of CdO followed by a 300 Å film of SnO_2 on the CdO. This structure proved to be more stable than the CdO/ Cu_2O 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.

IV. SUMMARY AND DISCUSSION

Table II 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(0) at the interface is given. The heterojunction cell of CdO/ Cu_2O prepared at room temperature did not show any reduction to Cu(0) at the interface.

While it is not yet established whether these photovoltaic characteristics arise from Cu/ Cu_2O junctions or oxide heterojunctions, the contacts of Cu_2O with SnO_2 or In_2O_3 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 eV 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 heterojunction cells are important because they establish that the chemical reduction to Cu(0) at the interface can be avoided and that true heterojunctions of semiconductor oxides on Cu_2O can be

TABLE II

CHARACTERISTICS OF OXIDE HETEROJUNCTIONS WITH Cu_2O

$X / \text{Cu}_2\text{O}$	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
	—	—	—	—

prepared with suitable choice of conditions. The cell is stable over short periods of time so that reproducible measurements can be made over longer 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 $\text{CdO}/\text{Cu}_2\text{O}$ 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 $\text{CdO}/\text{Cu}_2\text{O}$ 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 (5). Suitable annealing procedures have been shown (6) to improve the quality of cuprous oxide single crystals.

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7. Thus far we have not observed any significant differences in photovoltaic results between single crystal Cu_2O and the polycrystalline Cu_2O , in which the grain size is $\sim 1\text{-}2\text{mm}$. This may be because of the processing techniques currently used. It may be that when better techniques are developed, some differences will show up between single crystal and polycrystalline material.
8. Figure 5 should be compared with Figure 16. Note the jogs in the curve in Figure 5 indicated by the arrow denoting $\text{Cu}(0)$ and the absence of this feature in Figure 16.

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