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CUPROUS OXIDE PHOTOVOLTAIC CELLS

Technical Progress Report; January 1—May 31, 1978

By
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June 1978

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

Wayne State University
Detroit, Michigan

U.S. Department of Energy

MASTER

Solar Energy

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for period January 1, 1978 to May 31, 1978

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INTRODUCTION

It has been demonstrated that photovoltaic cells can be made from cuprous oxide, Cu_2O . Cuprous oxide is a p-type semiconductor with a band-gap of 2.0 eV, which is within the suitable range for photovoltaic cells for solar energy conversion. Cuprous oxide is an attractive material for low cost photovoltaic cells for large scale terrestrial use because it is easily derived from copper which is an inexpensive and abundant material and in which the U.S. is self-sufficient.

The current research project at Wayne State University was originally supported by NSF from October, 1975 to September, 1977 and was monitored by ERDA and DOE from August, 1976. During 1977, the work was also supported by the International Copper Research Association. This work has been reported at the Semi-Annual Program Reviews (1-4), and at the IEEE Photovoltaic Specialists' Conference (5,6) and other national and international meetings. The present phase is being supported by DOE-Photovoltaics from January 1 to July 31, 1978.

The previous work was largely devoted to front-wall Schottky barrier cells of Cu_2O . The polycrystalline Cu_2O sheets for these cells are prepared by oxidation of Cu in air at 1000°C . These can be converted into thin single crystals by the grain growth process. (7) The conductivity of the Cu_2O is improved by an anneal in air at 500°C followed by quenching. The best surface treatment is an etch in 8M HNO_3 followed by heat treatment in a vacuum before metallization in a vacuum.

Schottky barriers with a number of metals on Cu_2O were prepared and it was found that barrier height and the V_{oc} did not show a clear dependence

on the work function of the metal as might have been expected. (5) As an explanation it was proposed (3) that many of the metals of lower work function are also more active chemically than Cu and that they reduce the top surface of the Cu_2O to Cu thus creating a Cu/Cu $_2$ O contact. This limits the barrier heights to that of the Cu/Cu $_2$ O junction, ~ 0.65 eV and the V_{oc} to ~ 0.35 V. Some recent tentative results (4) showed that a few cells with an oxide interlayer between the metal and Cu $_2$ O gave a higher V_{oc} . While these cells represent an MIS structure which could explain the higher V_{oc} , it is also possible that the oxide interlayer acts to restrain the chemical reaction so that the greater band bending with the lower work function metals is retained to some degree. Initial explorations with Auger and ESCA surface studies (4) indicated that some of these questions could be usefully explored with these techniques.

OXIDE INTERLAYERS

The current emphasis on this project is on Metal-Cuprous Oxide photovoltaic cells with oxide interlayers e.g. Al/Al $_2$ O $_3$ /Cu $_2$ O structures which are referred to as MIS structures. As reported at the Semi-Annual Review Meeting of the Photovoltaic Advance Materials Program in Golden, Colorado in October, 1977 (4), several Al/Al $_2$ O $_3$ /Cu $_2$ O cells were prepared with $V_{oc} \sim 0.6-0.7$ V which is distinctly higher than the 0.35 V usually obtained with normal good cells of Cu/Cu $_2$ O or Al/Cu $_2$ O. The I-V characteristics of these cells are shown in Figure 1.

Al Oxide Interlayers: Attempts are being made to reproduce these results with improved equipment and techniques, but, although some modest improvements in V_{OC} have been found, no cells have recently been prepared with V_{OC} as large as the early cells.

The early procedure consisted of starting with annealed grain-growth Cu_2O sheets, etch in 8M HNO_3 for 20 seconds, place in a vacuum chamber, evacuate to 5×10^{-5} torr, back-fill with O_2 to 10^{-2} to 10^{-3} torr (and close system), evaporate Al as metal (oxides of Al are formed), heat the sample to $100^\circ C$ (to complete oxidation of Al), cool to room temperature, evacuate to 5×10^{-5} torr, evaporate Al metal, apply grid contacts by a second Al evaporation.

A number of variations and presumed improvements of this procedure have been tried. A better thickness gauge was installed to allow closer control of thickness. The system was cleaned and a liquid nitrogen trap was re-activated. A constant flow of O_2 was maintained and various pressures of O_2 were used. In a closed system, the oxygen pressure was varied from 5×10^{-4} to 5×10^{-2} torr. In a flowing system, the O_2 pressure was varied from 10^{-3} to 3×10^{-2} torr. The heat treatment procedure was also varied. All possible combinations of heating the samples before, during, and/or after the oxide formation-evaporation were tried, with heat treatment temperatures from 75° up to $150^\circ C$. Heating the sample after the oxide formation-evaporation seemed to be the most useful procedure while the treatment temperature seemed to make little difference in the results, within the range studied.

The Al oxide thickness was varied from $10\text{\AA}$ up to $80\text{\AA}$. Thickness above $50\text{\AA}$ gave high resistance junctions. None of these revised procedures

has produced cells with V_{oc} as high as the original cells. By varying the oxygen pressure during the evaporation of Al to form AlO_x , a slightly higher V_{oc} of 0.38 V was obtained at $40 \mu O_2$ pressure. It was noted that a faint glow discharge occurred at this pressure in this experimental apparatus when the filament was heated. This may be significant. After the AlO_x deposition, the sample was heated in the O_2 atmosphere for 10 min at $200^\circ C$.

Cells with the $Cu/AlO_x/Cu_2O$ structure gave essentially the same results as $Al/AlO_x/Cu_2O$ cells. With a gold top contact to give $Au/AlO_x/Cu_2O$ structures some interesting results were obtained. With thin layers of oxide, $20-30\text{\AA}$, so that tunnelling can occur, the I-V curves, both in the light and in the dark resemble the curves obtained with Cu/Cu_2O Schottky barrier cells on the same substrate, as shown in Figure 2. With oxide thicknesses greater than $50\text{\AA}$, substantially higher cell resistances were obtained, and the cells resembled a high resistance ohmic contact, but with a small photovoltaic effect. These results can be explained by assuming that a thin Cu layer was formed on the Cu_2O at the AlO_x interface. This view is supported by Auger and ESCA studies of these structures, as reported below.

Silicon Oxide Interlayers: In attempts to prepare SiO_2 interlayers, SiO was evaporated in O_2 atmospheres under various conditions. The layers can be characterized as SiO_x with $1 \leq x \leq 2$. The best results were obtained by evaporation in 10^{-3} torr O_2 , followed by heat treatment of the sample at $200^\circ C$ for 10 min in the O_2 atmosphere. The best cell was made with an Al top contact and an SiO_x thickness of $20\text{\AA}$. This gave $J_{sc} = 2.4\text{mA/cm}^2$, $V_{oc} = 0.34$ V and $FF = 0.43$ for an unencapsulated cell.

Cells with SiO_x interlayers and Cu top contacts were also prepared. Higher J_{sc} was obtained with Cu contacts, up to 3.2 mA/cm^2 , but the V_{oc} was only 0.27 V . One of these cells, prepared on a Cu_2O substrate of zone refined material gave a cell resistance of 0.9Ω for 1 cm^2 , which is the lowest cell resistance we have observed for any Cu_2O photovoltaic device.

Antimony Oxide Interlayers: Some Sb_2O_3 interlayers were tried in Metal/ $\text{Sb}_2\text{O}_3/\text{Cu}_2\text{O}$ structures. The Sb_2O_3 was chosen for study because it has been used with good success in GaAs MIS cells and because the Sb_2O_3 can be evaporated directly rather than relying on oxidation during evaporation as in the Al in O_2 procedure. The Sb_2O_3 was prepared by precipitation from an acid solution of SbCl_3 by neutralization with NH_3 solution.

The best cells were obtained with an Al top contact i.e. $\text{Al}/\text{Sb}_2\text{O}_3/\text{Cu}_2\text{O}$. With $30\text{\AA}$ Sb_2O_3 as an optimum thickness, results were $V_{ov} \sim 0.22 \text{ V}$ and $J_{sc} \sim 2 \text{ mA.cm}^2$. The cell resistance was low unless the Sb_2O_3 thickness exceeded $50\text{\AA}$.

With $\text{Cu}/\text{Sb}_2\text{O}_3/\text{Cu}_2\text{O}$ cells the V_{oc} was lower, $V_{oc} < 0.1 \text{ V}$ and J_{sc} up to 2.6 mA/cm^2 . The cell resistances were low, $10 - 12 \Omega$ and appeared to be limited by the bulk resistance, finger contacts, etc. Preliminary barrier height calculations indicate that the barrier height for this junction was $\sim 0.5 \text{ V}$.

With $\text{Au}/\text{Sb}_2\text{O}_3/\text{Cu}_2\text{O}$, ohmic contacts were obtained as in the case with gold directly on Cu_2O . If the Sb_2O_3 thickness was increased, $> 50\text{\AA}$, rectifying junctions were obtained, but no photovoltaic effect was observed.

The cells with Sb_2O_3 resemble an MIS structure in electrical characteristics. There is evidence for the existence of a negative fixed charge in the Sb_2O_3 interfacial layer, which would reduce the effective

barrier height, thus resulting in a decrease in V_{oc} . The work function of the metal also plays a role in determining the electrical characteristics, i.e., lower work function metals tend to yield a better V_{oc} while Au gives an ohmic contact.

IMPROVEMENTS IN CONDUCTIVITY OF Cu_2O

Since one of the factors limiting the J_{sc} and FF is the bulk resistivity of the Cu_2O , several approaches were explored to improve the conductivity of the Cu_2O . These were 1) variations in annealing, 2) zone refining and 3) doping.

Annealing Treatments: Because of variations in the observed cell resistances and in the resistivity of the grain growth Cu_2O plates, the preparation and testing procedures were reinvestigated and improved. A $500^\circ C$ anneal for 3 hours was found to be optimum but appeared to be more successful on thinner plates. Therefore the annealing was done after grinding and polishing the plates. Contacts were also improved by using evaporated Au contacts built up with Ag paint. These procedures consistently give plates with $\rho \sim 100 - 200 \Omega \text{ cm}$.

Zone Refining: A method for the zone refining of Cu_2O has been developed in this laboratory using a float zone method. This is quite effective in removing the impurities in the Cu_2O prepared from copper of the CD 110 grade. The impurities found by emission spectroscopy in the starting material are Mg, Si, Ag, Fe and Cr. These were reduced by zone refining to concentrations below the limits of analytical determination by Atomic Absorption Spectroscopy (0.15-2.5 ppm). The removal of Fe was followed in the most detail and it was established that the segregation coefficient

is < 0.001 . Zone refining appears to be beneficial in improving the properties of the Cu_2O since the resistivity after a 500°C anneal was found to be $\sim 35 \Omega \cdot \text{cm}$, lower than obtained with normal annealed grain growth material. Successful photovoltaic cells could be made with this zone refined material with results as good as the normal best cells, by present procedures.

Doping of Cu_2O : One method tried for introducing dopants into Cu_2O was to deposit the dopant metal on copper sheets and then to oxidize the Cu sheet in air at 1010°C . Cadmium and indium were found to be effective dopants. The Cd-doped Cu_2O has a $\rho \approx 150 \Omega \cdot \text{cm}$ as compared to 10^4 - $10^5 \Omega \cdot \text{cm}$ for grain growth Cu_2O (both as grown, without further annealing).

Another method of doping has been developed based on the use of a self-crucible technique in an arc image furnace. The self-crucible technique is used to avoid crucible contamination. In this method, a known amount of CdO was mixed with chunks of Cu_2O (prepared by oxidation of CD 110 copper rods), contained in a copper cup, and the top of the mass was melted in the focal point of the arc image furnace. The melt was poured into another copper cup. In this way, several disks of doped Cu_2O were prepared.

The resistivity of the samples as measured, and the amounts of Cd added and found by analysis are shown in Table I.

TABLE I

	Cd added (Wt. %)	Cd found by AA spectroscopy (Wt. %)	resistivity $\Omega \cdot \text{cm}$
I	0.066	0.011	1000
II	0.50	0.60	350
III	2.48	0.92	9

The resistivity of $9 \Omega \cdot \text{cm}$ appears to be the lowest yet reported for Cu_2O . Several $\text{Cu}/\text{Cu}_2\text{O}$ Schottky barrier cells were made by the normal procedures. However these cells did not exhibit any rectification and photovoltaic characteristics. Presumably new surface preparation procedures will have to be developed to utilize this material.

AUGER AND ESCA STUDIES

When a variety of Metal/ Cu_2O junctions were examined, it was found that the barrier heights did not vary greatly and did not correlate with the work function of the metal. We hypothesize that many metals can react chemically with Cu_2O to produce a surface layer of Cu metal so that many of the cells revert to being $\text{Cu}/\text{Cu}_2\text{O}$ junctions. It is hoped that the effect of the Al_2O_3 interlayer is to prevent this reaction. To test these hypotheses, a number of structures were examined by Auger and ESCA techniques. Depth profiles were made by sputter etching, and estimates were made of the relative amount of the various atomic species as a function of depth. Procedures were developed, using the fine structure of the Auger spectra of Al and Cu, to distinguish between the various valence states of these two metals, and to measure quantitatively the relative percentages of the different states.

When the ESCA technique is applied to normal cuprous oxide surfaces, the Auger LMM recoil electron is emitted at an energy of 337.5 eV (Mg K_α X-rays are used as the exciting radiation). A high resolution scan of this region of the ESCA spectrum is shown in Figure 3. When the cuprous oxide is reduced to copper metal, i.e. Cu (I) atoms are reduced to Cu (0), the additional electron in the M shell slightly reduces the recoil energy

of the emitted Auger electron to 335.8 eV. This makes it possible to distinguish between the two species of Cu and to obtain a quantitative estimate of the relative amounts of the two forms present. A similar technique is possible for the Al(0)-Al(III) system using the ESCA Aluminum 2p photoemission peak. Under the same X-ray excitation conditions, the Al(0) 2p emission occurs at 74.7 eV while the loss of three electrons to form Al(III) shifts the peak to 76.3 eV.

It was verified first that the sputter etch procedure did not generate any Cu metal. A Cu_2O surface etched with 8M HNO_3 did not show any surface Cu(0) or Cu(II). This showed that the etching procedure did not give a Cu/ Cu_2O junction. Since after a sputter etch, no Cu(0) or Cu(II) signal appeared, this showed the sputter etch treatment did not produce artifacts.

Figure 4 shows a depth profile of a Cu/ Cu_2O junction prepared by our usual procedure of vacuum evaporation of Cu onto Cu_2O . This shows Cu(0) on the surface and the Cu(I) of Cu_2O appearing at the sputtered depth of 20Å, a depth which corresponds to the amount of Cu metal laid down.

Figure 5 shows the results on an Al/ Cu_2O cell. Below the top layers, the Al metal, Al(0) decreased with depth, from 30 to 80Å, the Al(III) builds up over this region and copper metal, Cu(0) appears increasingly from 60 to 110Å. The Cu(I) of the bulk Cu_2O begins to appear at 110Å. This appears to be evidence for the postulated chemical reaction between Al and Cu_2O to form Cu and Al_2O_3 . Thus the hypothesis proposed earlier appears to be confirmed.

Figure 6 shows a profile of an Al/Al₂O₃/Cu₂O cell. In the intermediate region of 60 - 90 Å some Al(0) and Cu(0) are shown. This could perhaps be explained by assuming that the evaporation of Al in O₂ does not produce pure Al₂O₃ but rather Al mixed with Al₂O₃ due to incomplete oxidation. The Al can then react with the Cu₂O to produce a surface layer of Cu metal. The amount of Cu(0) produced is less than in the Al/Cu₂O junction.

Auger-ESCA profile studies were made on AlO_x/Cu₂O structures without a top metal contact. Again Cu(0) was found at the interface. This indicates that the method of producing the aluminum oxide, which was presumed to produce Al₂O₃, leads to a chemical reaction at the interface resulting in a production of Cu(0).

While the experiments were limited and exploratory, it has been established that the Auger and ESCA techniques can give significant and important results in these systems. We hope to be able to expand on these studies by cooperation with Dr. L.L. Kazmerski of SERI. These exploratory studies were done in a local industrial laboratory but the access to the equipment is limited. However, there are some installations in universities in the region to which we may be able to get access.

It appears that the main problem is that the evaporation of Al in an O₂ atmosphere does not give pure Al₂O₃ and that some Al metal is co-deposited in the film. This Al metal apparently reacts with the Cu₂O to produce the Cu surface and this causes the V_{oc} to degrade to the value of the Cu/Cu₂O junction. It is proposed, therefore, to concentrate on studies of the methods of deposition of Al₂O₃. One possible clue to the successful early results is that a glow discharge occurs in the evaporation

system under certain conditions, and this may insure the complete oxidation of the Al. This is currently under investigation. A somewhat related method is the gaseous anodization of Al in an O_2 glow discharge reported by Miles and Smith (8) and by Tibol and Hull (9). Also there are chemical methods for depositing Al_2O_3 , e.g. thermal decomposition of Al alkoxides. Other chemically deposited oxides could usefully be explored, e.g. as given by Powell, Oxley and Blocher (10). A recent method for the low temperature deposition of TiO_2 from Ti isopropoxide was described by Hovel (11).

OTHER ITEMS

Proposal: It is planned to submit a proposal on the PRDA for Evaluating the Potential of Less Developed Materials for Low Cost Solar Cells with Efficiencies of 10% or Greater, which is due July 6, 1978

Project Personnel: The Principal Investigators are Dan Trivich, Professor of Chemistry and Edward Y. Wang, Professor of Electrical Engineering. Dr. Richard J. Komp has rejoined the project as a full-time Research Associate. Anand Kakar, a graduate student in chemistry, continues on the project, with a nominal transfer from INCRA support. Mr. Ken Wang, a graduate student in Electrical Engineering has left and has been replaced by Mr. James Kotz, a graduate student in Physics.

Publications and Papers: In addition to the presentation at the Semi-annual Program Review in Golden, Colorado, on October 4-6, 1977, a paper was presented at the Electrochemical Society Meeting in Atlanta, October 9-14, 1977. Under the NATO collaboration with groups in Strasbourg, France, and Thessalonika, Greece, two papers were presented at the Photovoltaic

Solar Energy Conference in Luxembourg on September 27-30, 1977

(presented by Dr. C. Schwab of Strasbourg and Professor N.A. Economou of Thessalonkia). The full papers will be published in the Proceedings of the Conference.

A paper was presented at the American Ceramic Society Meeting in Detroit, May 6-11, 1978, and one at the IEEE Photovoltaic Specialists Conference in Washington, June 5-8, 1978.

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CURRENT VOLTAGE CURVES FOR $\text{Al}/\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$ PHOTOVOLTAIC CELLS

Figure 2. Current-voltage curves for $\text{Cu}/\text{Cu}_2\text{O}$ and $\text{Au}/\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$ cells.

Figure 3. High resolution ESCA spectrum showing Cu(0) and Cu(I) peaks.

Figure 4. ESCA-Auger depth profile of a Cu/Cu₂O Schottky barrier.

Figure 5. ESCA-Auger depth profile of a Al/Cu₂O Schottky barrier.

Figure 6. ESCA-Auger depth profile of a Al/Al₂O₃/Cu₂O metal-insulator-semiconductor structure.