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CUPROUS OXIDE PHOTOVOLTAIC CELLS

Final Report, January 1, 1978 to September 30, 1978

By
Dan Trivich
Edward Y. Wang
Richard J. Komp

October 1978

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

Wayne State University
Detroit, Michigan

U.S. Department of Energy

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Solar Energy

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CUPROUS OXIDE
PHOTOVOLTAIC CELLS

Final Report
for period
January 1, 1978 to September 30, 1978

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Prepared For

THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT ET-78-S-02-4726

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SUMMARY
OF FINAL REPORT CO-4726-10
ON "CUPROUS OXIDE PHOTOVOLTAIC CELLS"
DOE CONTRACT ET-78-S-02-4726
FOR PERIOD OF JANUARY 1, 1978 TO SEPTEMBER 30, 1978
BY
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Introduction: The objective of this research is to develop low cost photovoltaic cells based on cuprous oxide, Cu_2O , which is an inexpensive and highly available material. Previous work, which dealt with Schottky barrier Cu_2O cells, was sponsored by NSF and has been reported in an NSF Final Report, dated July, 1978, under contract NSF-AER-75-23453. The previous work indicated that limitations in the Schottky barrier cells could be due to chemical degradation at the junction. The objective of the present research was 1) to investigate the chemical character of the interface region to detect possible reactions 2) to investigate the effect of oxide interlayers in restraining reactions at the interface and to investigate the properties of the resulting MIS structures and 3) to explore other possible approaches to attaining improved efficiency. The chemical character of the interfaces was to be investigated primarily by Auger and ESCA surface analysis methods.

Present cells have an efficiency of 1.1% ($J_{sc} = 7.5 \text{ mA/cm}^2$, $V_{oc} = 0.35 \text{ V}$ and $FF = 0.45$) compared with theoretical values of $> 13\%$ ($J_{sc} = 17 \text{ mA/cm}^2$, $V_{oc} \geq 1.0 \text{ V}$, $FF = 0.8$)

Preparation of Cells: The basic method of preparation is to oxidize Cu sheet in air at 1000°C , anneal at 500°C to optimize the conductivity, grind and polish, etch in 8M HNO_3 , heat treat in vacuum, and apply oxide and metal coats by evaporation in vacuum or low oxygen pressure.

Improvements in Conductivity of Cu_2O : Experiments with annealing showed the highest conductivity is obtained by annealing at 500°C , preferably on thin samples. This gives $\rho \sim 100 - 200 \Omega \text{ cm}$. Float zone refining of Cu_2O is successful in removing impurities to levels below

~ 1 ppm. Zone refined material after 500°C anneal has $\rho = 35 \Omega \text{ cm}$. Doping of Cu_2O was achieved by coating Cu with metals before oxidation. Cadmium and indium were found to be effective. With Cd, $\rho \sim 150 \Omega \text{ cm}$. Doping of Cu_2O with $\sim 1\%$ CdO by melting gave $\rho \sim 9 \Omega \text{ cm}$.

Oxide and Other Interlayers: Because some cells of the type $\text{Al}/\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$ gave increased V_{oc} , the use of interlayers was investigated using Al_2O_3 , SiO_2 , Sb_2O_3 , and Si_3N_4 . It was concluded that the junctions containing AlO_x in recent cells also suffered chemical degradation because the method of deposition used (evaporation of Al in O_2) did not give complete conversion to Al_2O_3 . For SiO_2 , Sb_2O_3 and Si_3N_4 , the V_{oc} of the cells did appear to depend on the work function of the metal from Au to Ag to Al but the results were limited by other deficiencies in the films.

Auger and ESCA Studies: The hypothesis of chemical degradation of the junctions was investigated by high resolution Auger and ESCA methods with considerable success. It was shown that the high resolution methods can distinguish between Cu(I) as in Cu_2O and Cu(0) as in Cu metal. On $\text{Al}/\text{Cu}_2\text{O}$ junctions, Cu(0) was found at the junction which indicates that the Al reduced the Cu_2O to Cu thus producing a $\text{Cu}/\text{Cu}_2\text{O}$ junction which has a lower V_{oc} than would be expected from $\text{Al}/\text{Cu}_2\text{O}$. With AlO_x on Cu_2O , Cu(0) is also found at the interface, so that chemical reduction can be ascribed to residual Al in the incompletely oxidized AlO_x .

Conclusions: It has been established that chemical reactions at Metal/ Cu_2O junctions limit the barrier height and the V_{oc} of the cells to that of $\text{Cu}/\text{Cu}_2\text{O}$ junctions. Oxide and other interlayers may prevent this reaction and yield MIS structures with higher V_{oc} . Heterojunctions of Cu_2O with other oxides may be more promising in avoiding these reactions and may lead to superior cells.

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ABSTRACT

Cuprous oxide, with a band gap of 2.0eV, is a potentially useful material for photovoltaic cells because of low cost and high availability. Previous work on Schottky barrier Cu_2O cells indicated that the low efficiency of 1% could be due to chemical degradation of the junction. Interlayers could be useful in restraining this reaction and could lead to improved cells. In this research using Auger and ESCA surface analysis methods, it was found that copper metal was present at the junction in $\text{Al}/\text{Cu}_2\text{O}$ cells thus supporting the hypothesis of a chemical reaction between the Al and the Cu_2O . MIS cells with interlayers of SiO_2 , Sb_2O_3 and Si_3N_4 showed some dependence of V_{oc} on the work function of the metal but AlO_x interlayers, produced by evaporation of Al in O_2 , suffered the chemical degradation, presumably due to incomplete conversion to Al_2O_3 in the preparation. The resistivity of Cu_2O can be reduced by annealing at 500° ($\rho \sim 100 - 200 \Omega \text{ cm}$), by doping of Cu with Cd before oxidation to Cu_2O ($\rho \sim 150 \Omega \text{ cm}$), by zone refining and annealing ($\rho = 36 \Omega \text{ cm}$) and by doping of Cu_2O melts with CdO ($\rho = 9 \Omega \text{ cm}$).

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 research being presented in this report was supported by the Photovoltaics Division of the Department of Energy originally for the period of January 1, 1978 through July 31, 1978, with a no-cost extension to September 30, 1978. Previously the project research was 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 sponsored by the International Copper Research Association. This work has been reported at the Semi-Annual Program Reviews (1-4), at the IEEE Photovoltaic Specialists' Conferences (5,6) and other national and international meetings. Much of the work up to December 31, 1977 is described in a Final Report to NSF, under contract NSF-AER-75-23453, dated July, 1978

The previous work was largely devoted to front-wall Schottky barrier cells of Cu_2O . Schottky barriers with a number of metals on Cu_2O were prepared and it was found that the 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/Cu₂O contact. This limits the barrier heights to that of the Cu/Cu₂O junction, ~0.65 V 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 Cu₂O gave a higher V_{oc}, (see Figure 1). 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.

The purpose of the research presented in this report was 1) to investigate the chemical character of the interface region to detect possible reactions, 2) to investigate the effect of oxide interlayers in restraining reactions at the interface and to investigate the properties of the resulting MIS structures, and 3) to explore other possible approaches to attaining improved efficiency. The chemical character of the interfaces was to be investigated primarily by Auger and ESCA surface analysis methods.

BASIC METHOD FOR PREPARATION OF Cu_2O SCHOTTKY BARRIER CELLS

Since much of the work being reported derives from previous studies of Schottky barrier cells, it is useful to outline the basic method of the preparation of these cells. The general procedure consists of the following steps:

- (1) Oxidation of Cu sheet in air at 1000°C
- * (2) Conversion of Cu_2O sheet to single crystal by annealing in air at $1080\text{--}1120^\circ\text{C}$ to promote grain growth
- (3) Annealing of Cu_2O sheet in air at 500°C followed by quenching in water
- (4) Surface preparation by grinding and polishing
- (5) Etching in 8 M HNO_3 for 10-20 sec., followed by fast water rinse and drying
- (6) Vacuum treatment
 - ** (A) Heat treatment at $75\text{--}100^\circ\text{C}$ for 10 min.
 - (B) Application of thin metal coat by evaporation, e.g., Cu
 - (C) Application of grids by evaporation through a mask
- (7) Application of back contact, e.g., gold or silver paint
- (8) Measurement of I-V curves in dark and in light

(* Optional)

(** For Al coatings, the heat treatment may be omitted and replaced by an acetone rinse)

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°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 CDA 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 $\sim 35 \Omega \text{ cm}$, 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 $\rho \approx 150 \Omega \text{ cm}$ as compared to $10^4 - 10^5 \Omega \text{ cm}$ 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 CDA 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 $\Omega \text{ cm}$
I	0.066	0.011	1000
II	0.50	0.60	350
III	2.48	0.92	9

The resistivity of $9 \Omega \text{ cm}$ 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.

OXIDE AND OTHER INTERLAYERS

Al Oxide Interlayers: Attempts are being made to reproduce the results obtained previously with the aluminum oxide interlayer 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, grind with #400 alundum, fine grind with #600 alundum and 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, 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. Figure 2a shows a typical I-V plot for this type of cell.

The Al oxide thickness was varied from 10 Å up to 80 Å. Thickness above 50 Å 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 glowdischarge 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°C.

Cells with the $Cu/AlO_x/Cu_2O$ structure gave essentially the same results as $Al/AlO_x/Cu_2O$ cells (see Figure 2b). 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 Å, 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 3. With oxide thicknesses greater than 50 Å, 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 Å, as shown in Figure 4a. This gave $J_{sc} = 2.8 \text{ mA/cm}^2$, $V_{oc} = 0.34 \text{ V}$ 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. When gold was used as the top contact, essentially ohmic contacts were obtained with thin SiO_x interface layers. This is the same result as that of gold directly on Cu_2O . Figure 4c shows this result.

Antimony Oxide Interlayers: Some Sb_2O_3 interlayers were tried in Metal/ Sb_2O_3 / Cu_2O 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. Al/ Sb_2O_3 / Cu_2O . With 30 Å Sb_2O_3 as an optimum thickness, results were $V_{oc} \sim 0.27 \text{ V}$ and $J_{sc} \sim 2 \text{ mA/cm}^2$, (see Figure 5a). The cell resistance was low unless the Sb_2O_3 thickness exceeded 50 Å.

With $\text{Cu/Sb}_2\text{O}_3/\text{Cu}_2\text{O}$ cells (shown in Figure 5b), 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 $\text{Au/Sb}_2\text{O}_3/\text{Cu}_2\text{O}$, ohmic contacts were obtained as in the case of SiO_x interface cells (see Figure 5c). If the Sb_2O_3 thickness was increased, $> 50 \text{ \AA}$; rectifying junctions were obtained, but no photo-voltaic 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.

Silicon Nitride Interlayers: Silicon nitride (Si_3N_4) was tried as an insulating interlayer in MIS cells with Cu_2O . Silicon nitride can be sublimed or sputtered with RF according to MRC tables. The Si_3N_4 , being relatively stable, should not reduce the Cu_2O surface to Cu, as was found to occur with AlO_x .

The cells were prepared with the normal etched, heat-treated Cu_2O . The Si_3N_4 was sublimed from a closed boat. The top contact, applied by evaporation was of Cu, Ag, Au, or Al. The conditions of the Si_3N_4 sublimation caused erratic readings on the deposition monitor so that

the film thickness could not be determined with precision. Figure 6 shows the I-V curves obtained with these cells. With Au, substantially ohmic contacts were obtained indicating that reducing species were not present, so that reduction to Cu was avoided. For the others, the photovoltaic results were relatively poor with low J_{sc} and low V_{oc} . However, the V_{oc} did tend to increase with a decrease in work function of the metal, going from 0.025 V for Ag to 0.10 V for Cu and 0.18 V for Al. The values of J_{sc} were 0.06 mA/cm^2 for Ag, 0.05 for Cu and 0.11 for Al. The poorer results may have been due to interface states which may be avoidable by a change in conditions.

(7)
A paper by Wolff and Alcock indicates that at high temperatures, Si_3N_4 decomposes with a partial evolution of N_2 and that some oxidation can occur depending on the residual oxygen pressure in the system.

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 Cu/ Cu_2O 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 (X-Ray Photoemission, XPS) 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 and XPS 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 (see Figure 7) the Auger LMM recoil electron is emitted at an energy of 337.5 eV (Mg $K\alpha$ X-rays are used as the exciting radiation). A high resolution scan of this region of the ESCA spectrum is shown in Figure 13. 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, as shown in Figure 8. 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 emission peak. Under the same

X-ray excitation conditions, the Al(O) 2p emission occurs at 74.7 eV while the loss of three electrons to form Al(III) shifts the peak to 76.3 eV. Figure 9 shows a high resolution scan of this portion of the ESCA spectrum.

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(O) or Cu(II) (see Figures 10 and 11). This showed that the etching procedure did not give a Cu/Cu₂O junction. Since after a sputter-etch of 30 Å (as shown in Figures 12 and 13) no Cu(O) or Cu(II) signal appeared, this showed the sputter-etch treatment did not produce artifacts.

Figure 19 shows a depth profile of a Cu/Cu₂O junction prepared by vacuum evaporation of 50 Å Cu onto Cu₂O. The ESCA scan of the surface of the copper (Figure 14) shows the presence of a considerable quantity of cuprous oxide and oxygen. Some of this oxygen must be in the form of adsorbed water vapor or oxygen gas as there is twice the atomic percentage expected for the amount of Cu(I) atoms present. A small carbon signal is also seen. After an initial argon sputter-etch of 20 Å, the XPS signal shows virtually only copper metal, with trace amounts of O and Cu(I). A further etch of 30 Å (making a total of 50 Å removed) shows the return of the Cu(I) signal together with the proper atomic percentage of oxygen to indicate Cu₂O. A considerable amount of copper metal is still present. It was not possible to carry out simultaneous ion sputter-etching and Auger spectroscopy on these samples because of the need of obtaining a higher resolution spectrum of the copper LMM peak to determine the nature of the copper atomic species.

Therefore, the sputter-etching was carried out in stages with XPS measurements made each time after the system had been pumped back down to 10^{-8} torr. This is the reason for the limited number of data points.

Figure 20 shows the results of a depth profile on an Al/Cu₂O cell. The surface of the 70 Å thick vacuum evaporated aluminum metal top contact shows considerable oxidation of the Al caused by exposure of the cell to atmospheric pressure after preparation (see Figure 15). Again, the excess oxygen is probably adsorbed water vapor or oxygen gas. After ion sputter-etching 30 Å of the surface, the major portion of the aluminum is in the form of the metal, although considerable amounts of Al(III) and oxygen are still present. Below the top layers, the Al(O) decreases with depth, from 30 to 80 Å, the Al(III) builds up over this region and copper metal, Cu(O) appears increasingly from 60 to 110 Å. The Cu(I) of the bulk Cu₂O begins to appear at 110 Å.

Figure 16 is a high resolution spectrum of the Cu LMM Auger peak and shows the presence of the Cu(O) peak and the eventual appearance of the Cu(I) peak as sputter-etching was continued. Even when 150 Å was supposedly etched from the cell surface, Al(III) and Cu(O) were still detected. While it is possible that diffusion of the aluminum atoms into the bulk cuprous oxide may have taken place, a more plausible explanation is that slower sputter-etching occurred in the valleys of the highly textured surface produced by the chemical etching of cuprous oxide by nitric acid. The presence of the Cu(O) peak is evidence for the postulated chemical reaction between Al and Cu₂O to form Cu and Al₂O₃.

Figure 21 shows a profile of an $\text{Al}/\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$ cell. The top Al layer was 40 Å thick and the Al_2O_3 interface was 25 Å as measured by a quartz crystal thickness monitor in the vacuum evaporator. The outermost layer of this cell, as shown in Figure 17, looks substantially the same as the top of the $\text{Al}/\text{Cu}_2\text{O}$ cell. In the intermediate region of 60 - 90 Å some AlO and Cu(O) are shown. This could perhaps be explained by assuming that the evaporation of Al in O_2 does not produce pure Al_2O_3 due to incomplete oxidation. The Al can then react with the Cu_2O to produce a surface layer of Cu metal. The amount of Cu(O) produced is less than in the $\text{Al}/\text{Cu}_2\text{O}$ junction.

Auger-ESCA profile studies were made on $\text{AlO}_x/\text{Cu}_2\text{O}$ structures without a top metal contact. Again Cu(O) was found at the interface (see Figure 18). This indicates that the method of producing the aluminum oxide, which was presumed to produce Al_2O_3 , leads to a chemical reaction at the interface resulting in a production of Cu(O) .

It appears that the main problem is that the evaporation of Al in an O_2 atmosphere does not give pure Al_2O_3 and that Al metal is co-deposited in the film. This Al metal apparently reacts with the Cu_2O to produce the Cu surface and this causes the V_{oc} to degrade to the value of the $\text{Cu}/\text{Cu}_2\text{O}$ junction. This suggests that it may be useful to concentrate on studies of the methods of deposition of Al_2O_3 . 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 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 Blocker (10). A recent method for the low temperature deposition of TiO_2 from Ti isopropoxide was described by Hovel (11).

DISCUSSION

As a solar cell material, Cu_2O has the advantages of low cost and great availability. However, the present conversion efficiency of $\sim 1\%$ is too low for commercial use. Theoretical considerations indicate that efficiencies of 13% or greater are possible. The present results and theoretical possibilities are given in Table II.

TABLE II

(AMI)	PRESENT	THEORETICAL	POSSIBLE IMPROVEMENT
J_{sc}	7 mA/cm ²	17 mA/cm ²	2X
V_{oc}	0.35 V	1.0 V	3X
FF	0.45	0.8	1.5X
η	1.1%	13%	9.9%

As indicated, one could expect to increase J_{sc} by a factor of 2X, V_{oc} by 3X and FF by 1.5X for an efficiency goal of $\sim 10\%$. With heterojunctions a still larger V_{oc} may be possible, e.g. with $V_{oc} = 1.5$ V, the theoretical efficiency becomes 18%.

The J_{sc} can be improved by an improvement in diffusion length, which has been shown to depend on heat treatment as one factor, and by lowering the resistivity, which is achievable by purification, doping and heat treatment. Also improved light transmission through the top contact and anti-reflection coatings can give further improvement in J_{sc} . The fill factor is also improved by lowering the cell resistance.

The largest improvement could come from improvements in V_{oc} which would come from better junction formation techniques. The most important result of the present research is the evidence for a chemical reaction at the Metal/ Cu_2O junctions. The lower work function metals, which should produce higher barriers and higher V_{oc} , tend also to be more active chemically. Thus, in Al/ Cu_2O , the reaction $2 Al + 3 Cu_2O \rightarrow Al_2O_3 + 6 Cu$ apparently occurs, so that a Cu/ Cu_2O junction results.

Thermodynamic analysis can indicate which reactions are possible. The standard free energies of formation of several metal oxides are given in Table III together with the work function of the metals. These are arranged in order of decreasing stability of the oxides; the values are calculated to the common basis of the amount that consumes one mole of O_2 .

TABLE III

METAL	WORK FUNCTION	METAL OXIDE	$-\Delta G_f^\circ(298.15\text{ K})$ (kJ/mole O_2)
Mg	3.64	MgO	1139.1
Al	4.25	Al_2O_3	1050.9
Si	(4.01)	SiO_2	805.0
Cr	4.55	Cr_2O_3	697.9
Zn	4.24	ZnO	636.4
Sb	4.08	Sb_4O_6	415.5
Cu	4.47	Cu_2O	292.7
Ag	4.6	Ag_2O	216.4
Au	4.9	Au_2O_3	-108.8

It can be seen that a number of the low work function metals have oxides which lie above Cu_2O and are therefore more stable. Thus any metal whose oxide has a ΔG_f° more negative than Cu_2O can react to produce Cu. Whether the reaction does in fact occur depends on various kinetic factors, and these must be examined experimentally. The thermodynamic possibility of such reactions at junctions in solar cells is not unique with Cu_2O cells, and many other systems are susceptible to such changes in principle. For example, for an Al/ SiO_2 contact, thermodynamics predicts a possible reaction, so that in MIS structures with an SiO_2 layer and an Al top contact, the junction may deteriorate with time. Again, this rate is determined by kinetic factors.

For metal contacts on Cu_2O , it may be possible to restrain the reaction by use of a stable oxide interlayer. If the rates of the degradation processes are reduced sufficiently by this means, improved properties and adequate life may be achieved. This hypothesis was not adequately tested in this research in the case of aluminum oxide since the methods of depositing AlO_x appear to produce layers containing some residual reducing action. Probably better results can be obtained by direct sputtering of the oxide or by chemical deposition and it is planned to try these approaches.

In the case of the SiO_x , Sb_2O_3 , and Si_3N_4 interlayers, ohmic contacts were obtained with gold top contacts, and this indicates that there was no chemical reaction to produce Cu/ Cu_2O junctions in these structures. Hence these may be true MIS structures. The dependence of the open circuit potential on the work function for these cells, with aluminum contacts always yielding the highest V_{oc} , is an

indication that the Cu_2O base material is being protected from a chemical reaction with the Al. This shows that it may be possible to restrain the chemical reaction that degrades the Schottky barrier cell. However the open circuit potentials observed in these cells are smaller than those produced by a good $\text{Cu}/\text{Cu}_2\text{O}$ Schottky barrier. This could be caused by surface recombination taking place at the interface, as indicated also by the low J_{sc} observed in these cells. Also the lower V_{oc} could be due to negative fixed charges in the interfacial layers, since these would tend to lower the barrier height. Also these materials have a relatively high electron affinity compared with the Cu_2O for which $\chi = 3.2$ eV. MIS cells with interlayer materials of lower electron affinities than Cu_2O may produce better cells.

Another and perhaps more useful direction of future research would be to use heterojunctions of oxides on Cu_2O since these would not be subject to chemical degradation. Some preliminary investigations on such systems have been reported by us (3). ZnO appears to be the most promising material. Selection of other materials would require that they be n-type and have a low electron affinity, with band gaps greater than 2 eV and have a compatible crystal structure and lattice parameter.

CONCLUSION

Some important limitations on the development of Cu_2O Schottky barrier solar cells have been found through Auger and ESCA surface analysis methods which show that certain Metal/ Cu_2O junctions degrade by chemical reactions. It may be possible to avoid these degradations and thereby achieve improved Cu_2O cells through the use of oxide interlayers in MIS structures or through the use of oxide heterojunctions.

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Fig. 1 CURRENT VOLTAGE CURVES FOR AL/AL₂O₃/Cu₂O PHOTOVOLTAIC CELLS

Fig. 2a

Al/Al₂O₃/Cu₂O

Fig. 2b

Fig. 2 CURRENT-VOLTAGE CURVES FOR METAL/Al₂O₃/Cu₂O PHOTOVOLTAIC CELLS

Fig. 3 CURRENT-VOLTAGE CURVES FOR $\text{Cu}/\text{Cu}_2\text{O}$ CELLS COMPARED TO $\text{Au}/\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$ PHOTOVOLTAIC CELLS

Fig. 4a

Al/SiO_x/Cu₂O

Fig. 4b

Fig. 4 CURRENT-VOLTAGE CURVES FOR METAL/SiO_x/Cu₂O PHOTOVOLTAIC CELLS

Fig. 4c

Fig. 4(cont.) CURRENT-VOLTAGE CURVES FOR METAL/SiO_x/Cu₂O
PHOTOVOLTAIC CELLS

Fig. 5a

Fig. 5b

Fig. 5 CURRENT-VOLTAGE CURVES FOR METAL/Sb₂O₃/Cu₂O PHOTOVOLTAIC CELLS

Fig. 5c

$\text{Au} / \text{Sb}_2\text{O}_3 / \text{Cu}_2\text{O}$

Fig. 5d

Fig. 5(Cont.) CURRENT-VOLTAGE CURVES FOR METAL/ Sb_2O_3 / Cu_2O PHOTOVOLTAIC CELLS

Fig. 6a

Fig. 6b

Fig. 6 CURRENT-VOLTAGE CURVES FOR METAL/Si₃N₄/Cu₂O PHOTOVOLTAIC CELLS

Fig. 6c

Fig. 6(Cont.) CURRENT VOLTAGE CURVES FOR METAL/ Si_3N_4 / Cu_2O PHOTOVOLTAIC CELLS

Fig. 7 ESCA SPECTRUM FOR CLEAN Cu_2O SURFACE

Fig. 8 HIGH RESOLUTION ESCA SPECTRUM SHOWING SHIFT IN Cu LMM AUGER LINE FOR Cu(I) COMPARED TO Cu(0)

Fig. 9 HIGH RESOLUTION ESCA SPECTRUM SHOWING SHIFT IN Al 2p XPS LINE FOR Al(III) COMPARED TO Al(0)

Fig. 10 INITIAL ESCA SPECTRUM FOR Cu_2O SURFACE SHOWING SURFACE CONTAMINATION

Fig. 11 HIGH RESOLUTION ESCA SPECTRA OF Cu LMM AUGER LINE

Fig. 12 ESCA SPECTRUM FOR Cu_2O SURFACE AFTER 30 Å SPUTTER-ETCH

Fig. 13 HIGH RESOLUTION ESCA SPECTRUM OF Cu LMM AUGER LINE FOR Cu_2O SURFACE AFTER 30 Å SPUTTER-ETCH

Fig. 14 INITIAL ESCA SPECTRUM OF Cu/Cu₂O JUNCTION

Fig. 15 INITIAL ESCA SPECTRUM OF Al/Cu₂O JUNCTION

Fig. 16a HIGH RESOLUTION ESCA SPECTRA OF Cu LMM AUGER LINE OF Al/Cu₂O JUNCTION AFTER VARIOUS AMOUNTS OF SPUTTER-ETCH

Fig. 16b HIGH RESOLUTION ESCA SPECTRUM OF Cu LMM AUGER LINE OF Al/Cu₂O JUNCTION AFTER 150 Å OF SPUTTER-ETCH

Fig. 17 INITIAL ESCA SPECTRUM OF $\text{Al}/\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$ JUNCTION

Fig. 18 HIGH RESOLUTION ESCA SPECTRUM OF Cu LMM AUGER LINE OF $\text{Al}_2\text{O}_3/\text{Cu}_2\text{O}$ JUNCTION AFTER 100 Å SPUTTER-ETCH

Fig. 19 ESCA DEPTH PROFILE OF Cu/Cu₂O JUNCTION

Fig. 20 ESCA DEPTH PROFILE OF Al/Cu₂O JUNCTION

Fig. 21 ESCA DEPTH PROFILE OF Al/Al₂O₃/Cu₂O JUNCTION