JNSF 16-1-125

J. Natn. Sci. Coun. Sri Lanka 1988 **16** (1) : 125–129

n – TYPE ELECTRICAL CONDUCTIVITY IN CUPROUS OXIDE THIN FILMS

W. SIRIPALA AND K. P. KUMARA
Department of Physics, University of Kelaniya, Kelaniya, Sri Lanka.

(Date of receipt : 09 September 1987)
(Date of acceptance : 26 January 1988)

Abstract : Electrodeposited cuprous oxide thin films were investigated to determine whether their electrical conductivity is n-type or p-type. The experimental results based on the measurements of thermoelectric e.m.f., sheet resistance, dark and light current – voltage characteristics of Cu_2O/Cu_xS and Cu_2O/CuCNS heterojunctions reveal that the electrodeposited cuprous oxide films produce n-type electrical conductivity. These observations are in very good agreement with the previously reported n-type behaviour of the electro-deposited Cu_2O film electrodes in a photoelectrochemical cell.

1. Introduction

Cuprous oxide (Cu_2O) is an attractive material for photovoltatic energy conversion because it has a band gap of 2.0 eV and it is less expensive compared to many semiconducting materials. Experimental and theoretical studies of Cu_2O solar cells have been reported previously.[1,2,3,4] However, the experimentally obtained efficiencies were much less than the theoretically predicted value. Moreover, all the work reported were based on the p-type semiconducting Cu_2O only. Many authors have claimed that the efficiency of Cu_2O solar cells may be improved significantly if a homojunction could be developed provided that the n-type Cu_2O is possible.[5] Nevertheless, n-type photoconductivity of Cu_2O has been reported previously using the photoelectrochemical methods.[7,8] In this investigation, we have undertaken several experiments, other than photoelectro-chemical, to verify the n-type behaviour of the electrodeposited Cu_2O films. Our experimental investigation reveals that the n-type conductivity is possible in electrodeposited Cu_2O films.

2. Experimental

Cuprous oxide thin films were deposited on various metal substrates (Cu, Ti, Pt) using the previously described electrodeposition technique.[8] The metal plates were used as cathodes in an electrochemical cell containing an aqueous solution of 0.01 M $CuSO_4$ with an added few drops of NaOH, while a carbon rod was used as the anode. The electrodeposition was carried out for about 1 hour under the constant current density of 10 mA/cm^2. However, for Cu substrates simple dipping of the samples in the electrolyte for about 8 hours was sufficient to produce samples with considerable thickness of Cu_2O films. Most of the measurements in the investigation were carried out for the samples prepared on Cu substrate using the dipping method. However, we have found that the experimental results were the same for all the samples prepared on different metal substrates, but the magnitudes varied somewhat from sample to sample.

Thermoelectric e.m.f measurements were obtained by keeping the substrate of the samples in thermal contact with an electric heater while the film surfaces were being exposed to air. Sheet resistance measurements were made using the conventional four-probe technique. The probes were made of gold plated copper wires and it was also ensured that the I–V characteristics being linear over the range used in these experiments.

Thin copper sulfide (Cu_xS) coatings were deposited on the Cu_2O films by spraying an ammonium sulfide solution (10% by volume) over the surface of Cu_2O films. However, thin CuCNS films were coated by immersing the Cu_2O samples in an aqueous electrolyte of 3M KCNS containing 5% (by volume) of acetic acid for about 2 seconds.[10] For both types of coatings, however, it was observed that the thicknesses of the coatings were crucial and overexposure would not produce the expected junction behaviour. Dark and light current – voltage measurements of the above samples were taken by making electrical contact to the front surface by using a mechanically pressed gold – plated copper wire. Back contact was made to the metal substrate. The light source was a 150 W tungsten – halogen lamp and the light intensity was measured with an International light IL 700 research radiometer.

3. Results and Discussion

Thermoelectric e.m.f measurements were obtained for both types of samples, namely the electrodeposited Cu_2O films on the various metal substrates and the thermally grown Cu_2O films on Cu substrates. Always the thermoelectric e.m.f values for electro-deposited samples were in opposite sign with the thermally grown samples, however, the magnitudes vary from sample to sample. This simple observation suggests that the majority carriers in the electrodeposited Cu_2O films are electrons, compared with the well established result of p-type carriers in the thermally grown Cu_2O films.

It is known that thermally grown Cu_2O films on Cu substrates produce Cu/Cu_2O Schottky contacts at the substrates. In our investigation we have given special attention to this contact effect, because, if the electrodeposited Cu_2O films also produce this effect then the interpretation of the heterojunction using the sheet resistance measurements and the photoeffect is questionable. Therefore, all the electrodeposited Cu_2O samples on various metal substrates were subjected to the sheet resistance measurements, and also to tests for the possible photoeffects. We have not observed any significant sheet resistance value, which suggests the shunting through the metal substrate in the absence of a junction, not any photoeffect. This result rules out any possible junction effects that might interfere with our experimental observations.

Sheet resistance values were obtained for the Cu_xS coated Cu_2O films and for the CuCNS coated Cu_2O films. These values were within the range of 500–1000 Ω/□ for both types of coating. However, the sheet resistance values of Cu_2O, Cu_xS and CuCNS films alone, prepared on the Cu substrates were negligible as mentioned previously. One possible way to explain the increase in sheet resistance is due to the fact that the shunting resistance of the surface layer is increased by the formation of a heterojunction. In general, this is the case if Cu_2O is n-type, since both Cu_xS and CuCNS are p-type. [7,9] Further evidence to the existence of a heterojunction is shown in Figure 1. The dark and light current – voltage behaviour of Cu_2O/Cu_xS junction clearly demonstrates the blocking nature of the junction, as well as the photoeffect. The decrease in the photosignal in the forward bias direction also clearly indicates the existence of a space charge layer at the junction which tends to vanish at forward condition. Although, Figure 1 shows the results of Cu_2O/Cu_xS junction, similar results were obtained for Cu_2O/CuCNS junction as well.

Thermoelectric e.m.f measurements directly suggest that the electrical conductivity of electrodeposited Cu_2O films is n-type. Observations of the possible existence of the heterojunction effects with Cu_xS and CuCNS p-type semiconductors also favour this suggestion. Furthermore, we have an another evidence for the n-type behaviour of Cu_2O films, namely, the observation of the n-type photoconductivity in electrodeposited Cu_2O films in a photoelectrochemical cell.[8] All these experimental evidences lead to the same conclusion that the electrical conductivity of electrodeposited Cu_2O films is n-type. However, the origin of this n-type behaviour is unknown and the possibility of oxygen vacancies and/or the additional copper atoms at the interstitial positions still to be examined.

4. Conclusion

In conclusion, the experimental evidences that we have presented here support the idea of the existence of n-type electrical conductivity in electrodeposited Cu_2O films. We also believe that the heterojunctions Cu_2O/Cu_xS and Cu_2O/CuCNS may be useful in developing inexpensive thin film solar cells. This will be the subject for our future investigations.

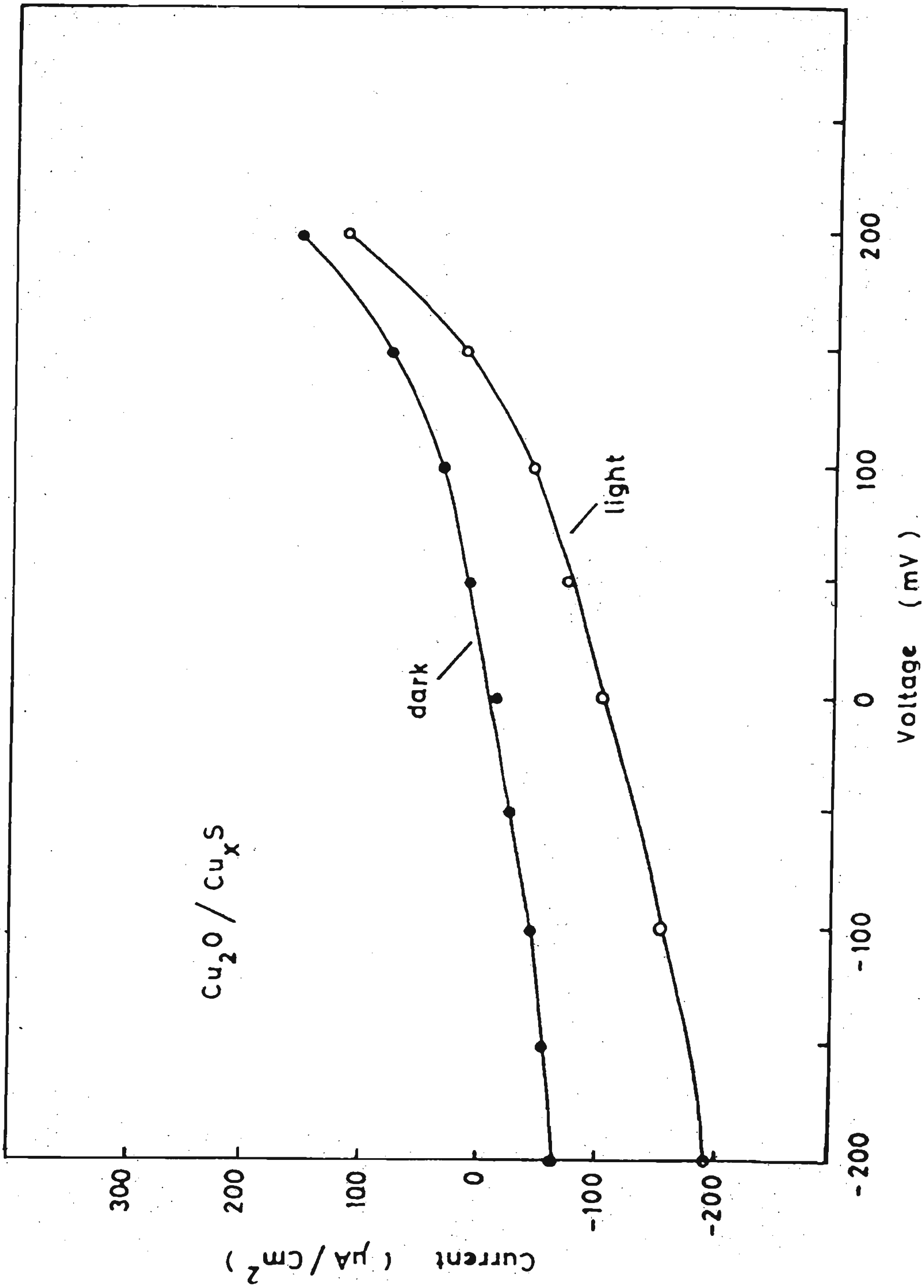

Figure 1. Light and dark current-voltage characteristics of Cu_2O/Cu_xS junction. Light intensity = 50 mW/cm^2

Acknowledgement

This work was supported by research grants from the Third World Academy of Sciences, Italy, and Natural Resources, Energy and Science Authority of Sri Lanka.

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