J. Natn. Sci. Coun. Sri Lanka 1990 18(2) : (109-117)

PHOTOVOLTAIC PROPERTIES OF Cu_2O/Cu_xS HETEROJUNCTION

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

(Date of receipt : 25 January 1990)
(Date of acceptance : 20 April 1990)

Abstract: A simple electrochemical method was developed to fabricate a Cu_2O/Cu_xS heterojunction and it was then used in preparing a thin film photovoltaic solar cell. Cu_2O was prepared by the method of electrodeposition and Cu_xS was coated on Cu_2O by a simple dipping method. The photovoltaic properties of the cell could be improved significantly by heat treatment in air. The maximum conversion efficiency of the cell was 0.1% and V_{oc} = 180 mV and I_{sc} = 2.0 mA/cm^2 under A M 1 artificial illumination.

1. Introduction

The search for low–cost solar energy converting devices through inexpensive solar energy materials has been a subject for many decades.[2,6,8] It has been very well established that inexpensive materials and simple processing techniques are the key factors that reduce the cost of production of photovoltaic solar cells. Nevertheless, the useful life time of a cell is also a very significant factor in determining the practical applications. Among many solar energy materials Cu_2O and Cu_2S have been considered to be the most inexpensive materials because their starting material copper is abundant and processing techniques are comparatively simple.[9,12] Indeed Cu_2S is being widely used in Cu_2S/CdS photovoltaic solar cells. Cu_2O has also been tested in Schottky unction and heterojunction solar cells. However, their efficiencies were limited.[1,7,13] Most of the reported work on Cu_2O is based on thermally prepared p–type Cu_2O and there is little work reported on other methods such as anodization, sputtering and electrochemical methods. Recently, it has been reported that there is a simple electrochemical method for preparing copper oxide films on copper and other metal substrates.[1,10,15] In this method metal electrodes are used as cathodes in a cell containing Cu^{++} ion aqueous solution to prepare thin Cu_2O films on the substrates. The important difference between this type of Cu_2O films and the thermally grown Cu_2O films is that these film electrodes always resulted enhanced n–type photosignals in photoelectrochemical cells compared to the p–type photosignals with thermally grown Cu_2O film electrodes.[1,10,15] This important behaviour of electrodeposited Cu_2O films was used in this investigation to prepare Cu_2O/Cu_xS heterojunction and study the photovoltaic properties to envisage the possibility of developing a low–cost thin film photovoltaic solar cell.

In our investigation, we have developed a simple electrochemical technique to fabricate the Cu_2O/Cu_xS heterojunction and used it to prepare a thin film photovoltaic solar cell. We have obtained the efficiency of 0.1%

with the cell parameters V_{oc} = 180 mV and I_{sc} = 2 mA/cm^2 under AM 1 illumination. We have also observed that the efficiency of the cell could be improved significantly by heat treatments in air . The stability of the cell was also good.

2. Experimental

Thin cuprous oxide films were deposited on copper substrates by the previously reported method of electrodeposition.[1,2] Copper plates (2x2 cm^2) were initially polished with sand paper and then washed, degreased and rinsed in distilled water and then dipped in an ammonium sulphide solution carried out at a constant current density of 10 mA/cm^2 with a copper anode and an aqueous electrolyte containing 0.3M cupric acetate. The temperature of the electrolyte was maintained at 80^{0}C and it was stirred contineously using a magnetic stirrer. 5 min. of electrodeposition was sufficient to obtain a uniform film with considerable thickness. This film was rinsed in distilled water and then dipped in an ammonium sulphide solution (1% by volume) at 70^{0}C for 2 sec. to prepare a uniform Cu_xS coating on Cu_2O. This was rinsed again in distilled water and then dried in air. A mechanically pressed platinum grid was used as the front contact of the cell while the back contact was made to the substrate.

Since prepared cells produced relatively low photoresponses, the cells were heat treated in air for different lengths of time at different temperatures, in order to improve the photovoltaic properties. Each time the light induced short–circuit current and the open–circuit voltage of the cell were monitored to find out the optimum values of the heat treatment temperature and the time. Light intensity was measured with an International Light IL 1350 Radiometer and current and voltages were measured with Keithly Model 197 digital multimeter.

Sheet resitance values of the films were measured using the conventional four–probe technique. Probes were made with a platinum wire and the separation between the probes was 2 mm and the contact area was 1 mm^2. The IV characteristics were linear over the ranges used in this experiment.

3. Results and Discussion

The variations of the short circuit current and the open circuit voltage with the duration of heat treatments at different temperatures are shown in Figure 1 and Figure 2. It can be clearly seen that the prolonged heat treatments would destroy the performance of the cell. However, there is an optimum time and temperature at which the cell produces the highest photoresponses. Unless otherwise stated we have heat treated the cells to this optimum value prior to the subsequent measurements. Figure 3 shows the dark and light current–voltage characteristics of the cell (a) before (b) after heat treatment. High rectification factor and high photoresponces are evident in heat treated cells. The short–circuited spectral response of the cell is shown in Figure 4.

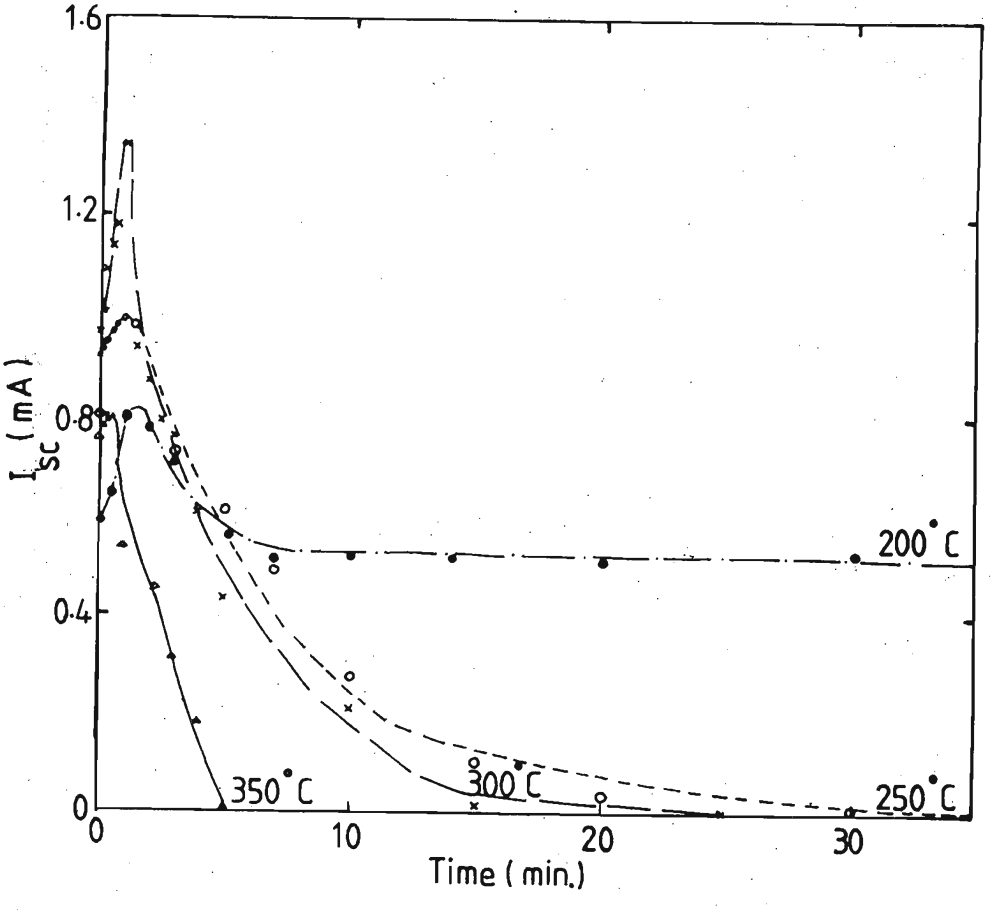

Figure 1 : Variations of the short circuit current of Cu_2O/Cu_xS cell with the duration of heat treatment in air at different temperatures. Intensity of illumination = 200 mw/Cm^2.

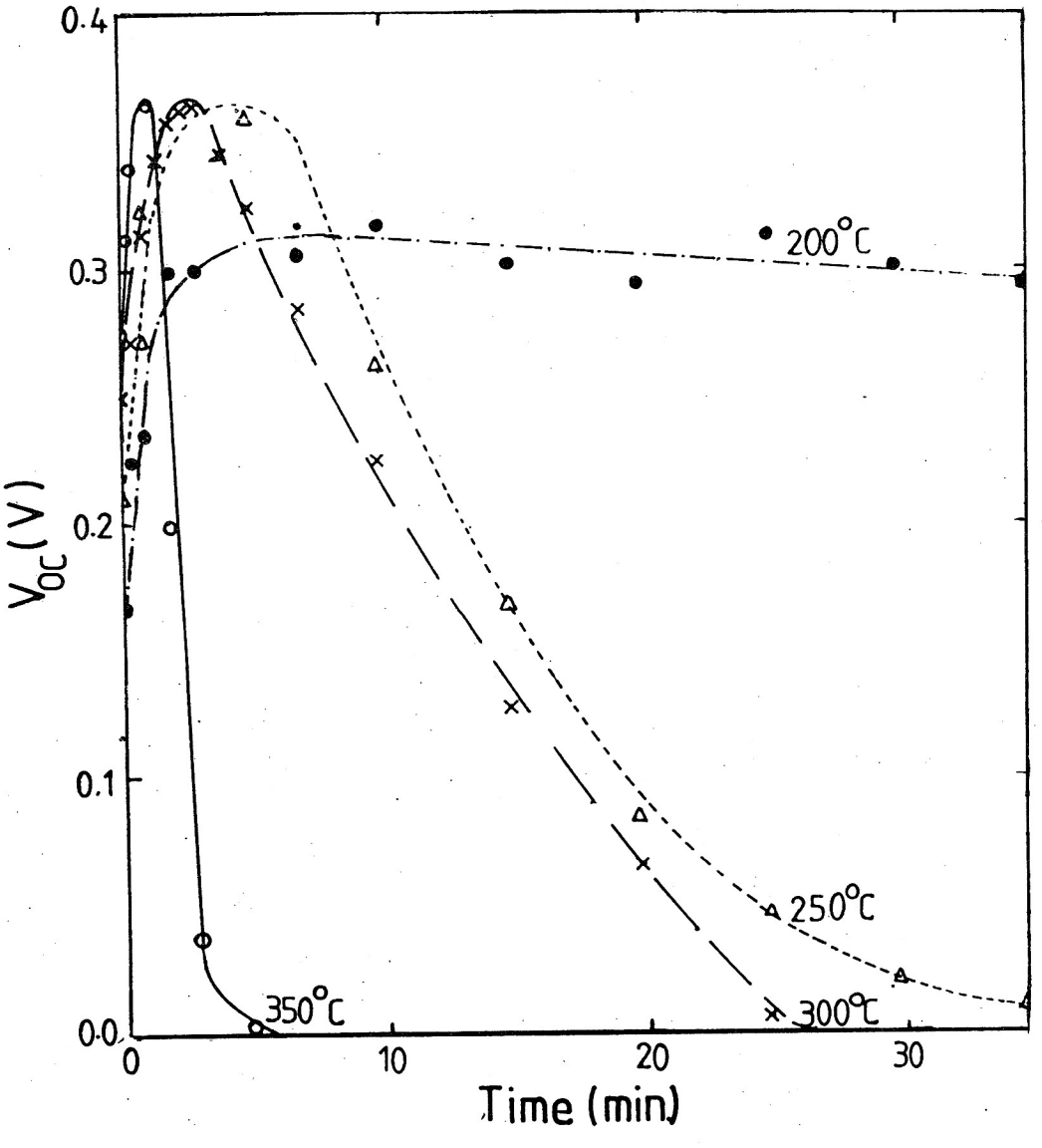

Figure 2 : Variations of the open circuit voltage of Cu_2O/Cu_xS cell with the duration of heat treatment in air at different temperatures. Intensity of illumination = 200 mw/Cm^2.

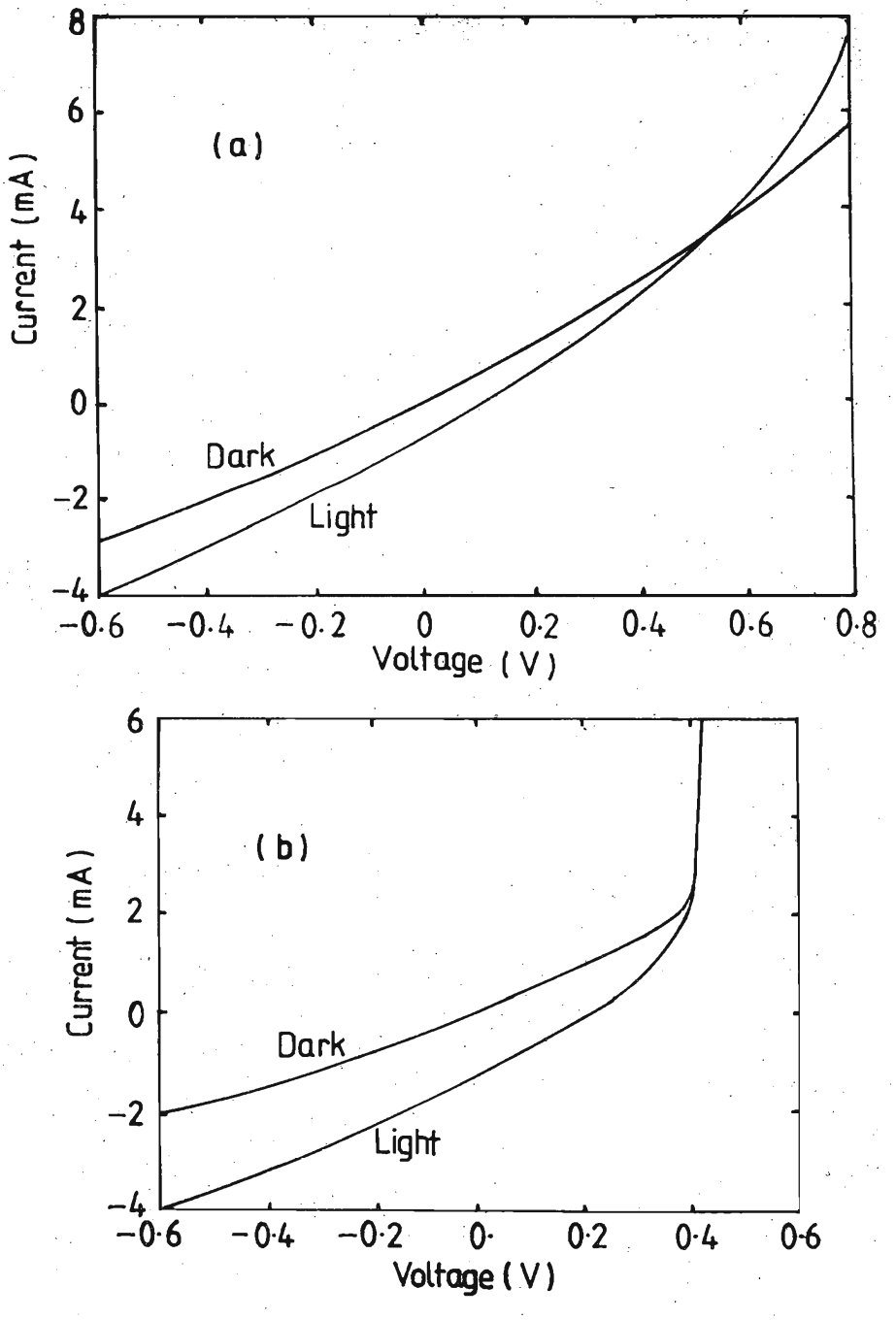

Figure 3 : Dark and light current voltage characteristics of Cu_2O/Cu_xS cell (a) before (b) after, heat treatment in air at 300^0C for 2 minutes.

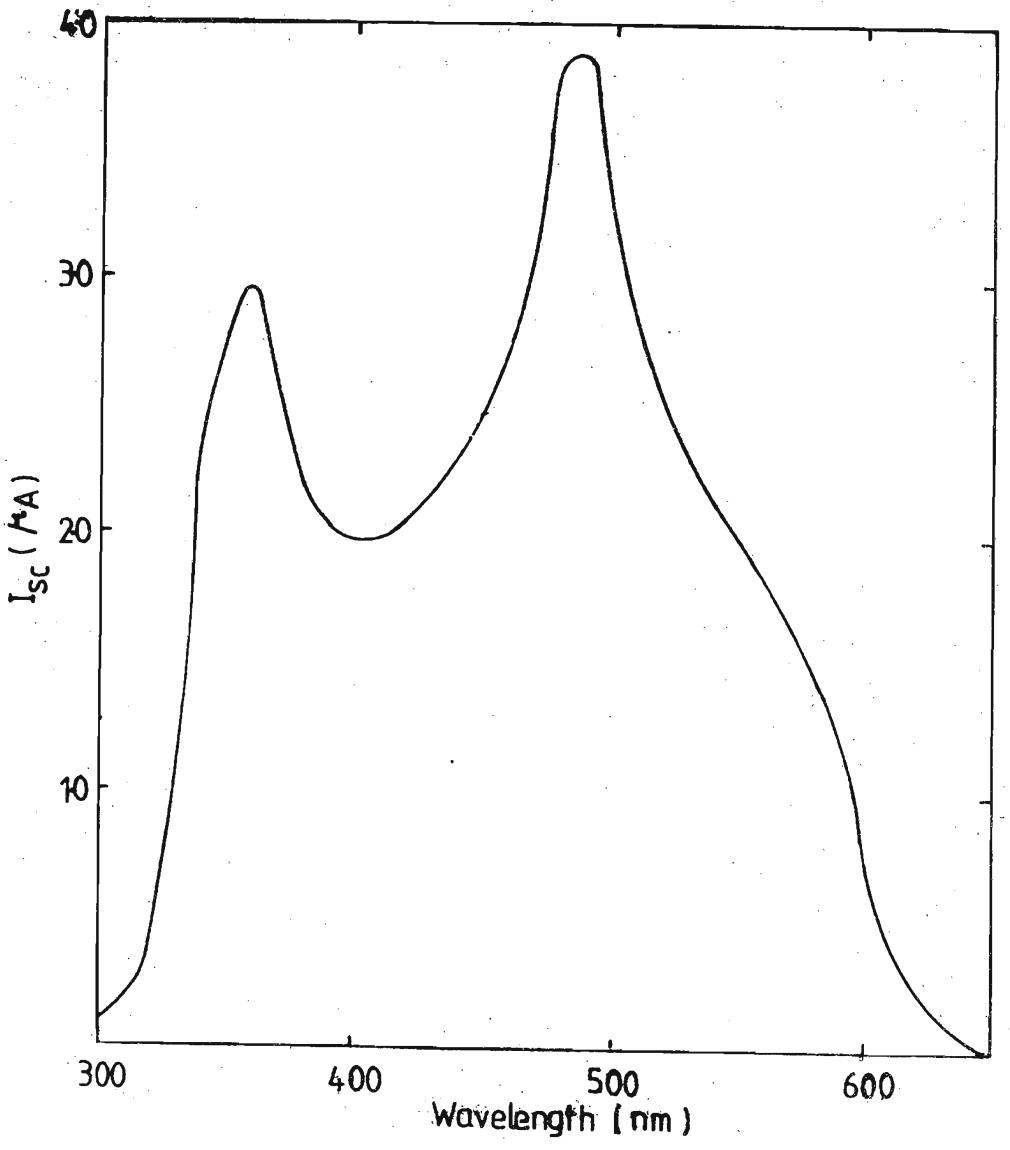

Figure 4 : Short circuit spectral response of Cu_2O/Cu_xS cell.

The photovoltaic characteristics of Cu_2O/Cu_xS cells were measured at 100 mW cm^{-2}. The effective cell area was 0.38 cm^2. The open circuit voltage and the short circuit current were 180 mV and 2.0 mA/cm^2 respectively. We have tested the stability of the cell in continuous illumination under the short circuit conditions. Periodically the open circuit voltage and the short circuit currents were monitored. We have repeated the experiment with an IR water filter to reduce the possible heating effects of the cell. The results are shown in Figure 5 and it is evident that the heating effects has also contributed to the initial decrease in photoresponse of the cell.

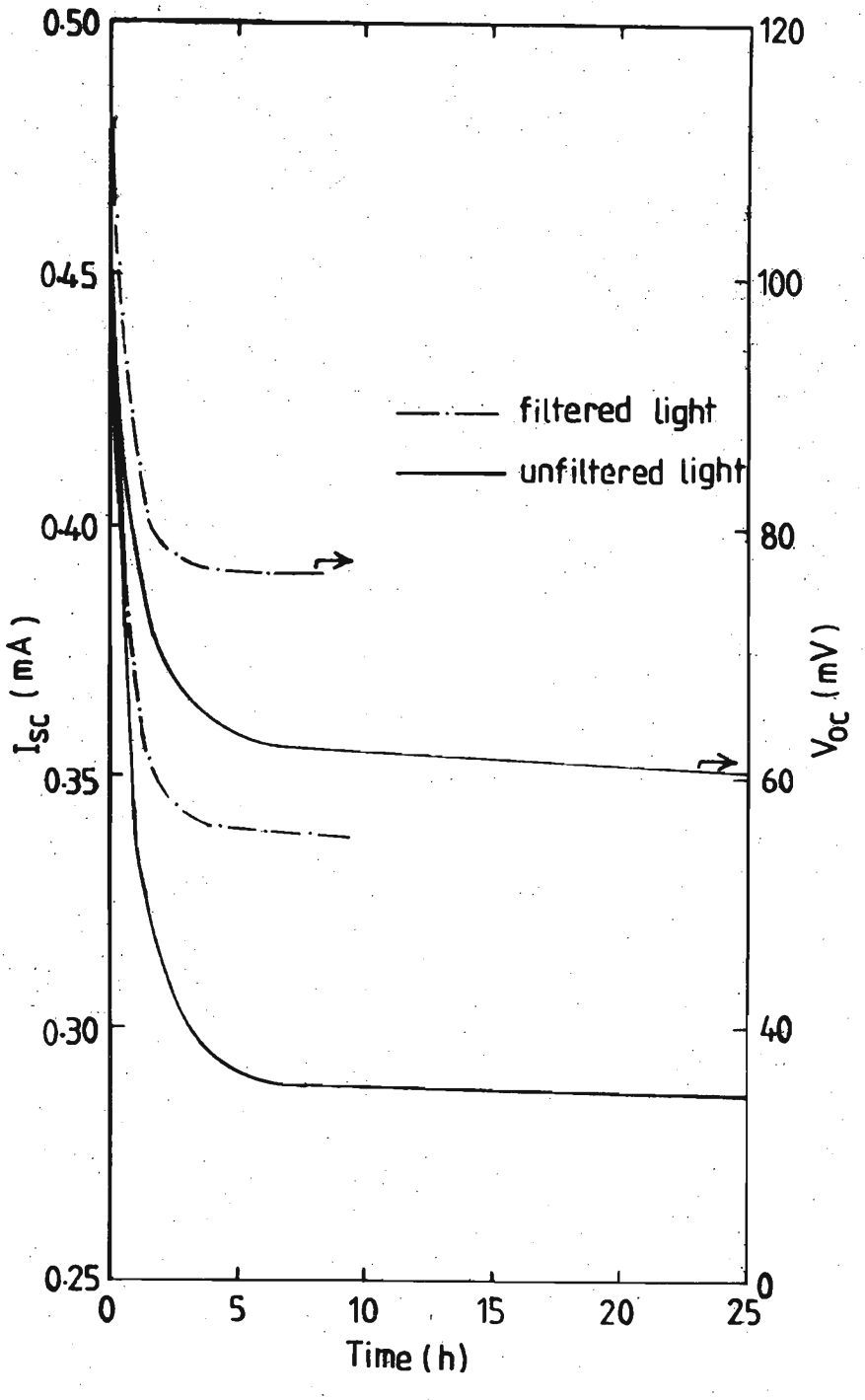

Figure 5 : Variations of short circuit current and open circuit voltage with time under the constant illumination of intensity 60 mw/Cm^2. Dotted line curves were obtained with an IR water filter.

Figures 1 and 2 clearly indicate that the photoresponse of Cu_2O/Cu_xS thin film cells could be improved significantly by proper heat treatments. Similar results have been reported earlier on CdS/Cu_xS thin film photovoltaic solar cells.[3,5] We have made use of the simple method of sheet resistance measurements in monitoring the changes in the Cu_2O/Cu_xS heterojunction upon heat treatment.[3] We first measured the sheet resistance of Cu_2O films coated on copper substrates and observed no significant resistance values (for the obvious reason of current shunting through the metal substrate) and this was true even after the films were heat treated. When Cu_xS film was coated on Cu_2O film the sheet resistance value increased to about 300 $\Omega/\square$ and this value reached about 1500 $\Omega/\square$ after the heat treatment (these values may vary somewhat from sample to sample, however, the order of magnitude remains the same). This result is a good indication that the shunt resistance of the Cu_2O/Cu_xS heterojunction may have increased upon the heat treatment. The increase in photoresponses as shown in figures 1 and 2 is also in favour of this idea. One important aspect of the heterojunction under the investigation is that the Cu_2O films are prepared by the method of electrodeposition and they produce n—type photosignals in photoelectrochemical cells irrespective of the well established result of p—type photosignals with thermally grown Cu_2O films. Indeed, the thermally grown Cu_2O films did not produce the enhanced photovoltaic effect ($V_{oc} \sim 1$ mV, $I_{sc} = 2\mu A$) and the increase in the sheet resistance values were also negligible, when they were coated with Cu_xS films. Therefore, the electrodeposited Cu_2O films may be creating a heterojunction with p—Cu_xS which is able to separate electron—hole pairs efficiently. The detailed nature of the junction characteristics of Cu_2O/Cu_xS is not the subject of this paper except the photovoltaic effect of the junction. Indeed, the exact band profile at the junction may be very useful in a detail study.

As shown in figure 5, both open circuit voltage and short circuit current decrease initially upon the continuous illumination. However, they become constant after some time. It is clear, as mentioned earlier, that the heating of the cell has also contributed to the initial decrease in photosensitivity. Other than the heating, the possibilities such as the charging of the defect traps[4,11,14] and long term changes in the chemical compositions of the materials[3] are not excluded at this stage. However, the important observation, in our opinion, is that the cell does not totally degrade upon the continuous illumination.

The conversion efficiency of the Cu_2O/Cu_xS thin film photovoltaic solar cell that we report here is 0.1%. Undoubtely this value is very low compared to many thin film solar cells. The reflection losses at the surface has not been accounted for in the calculation. On the other hand, the front contact made by mechanically pressing a platinum grid may be producing a series resistance to the cell and thereby limiting the efficiency. Also, the number of grid lines has not been optimized. Therefore, in considering the above factors, it can be seen that the cell efficiency can be increased further. Nevertheless, the maximum reported efficiency values of Cu_2O based

solar cells are limited to about 1%. In this regard, the efficiency value of 0.1% is encouraging.

4. Conclusion

In conclusion, we have shown that the simple electrochemical method could be used to fabricate a Cu_2O/Cu_xS thin film solar cell. Namely, Cu_2O films were prepared by electrodeposition technique and Cu_xS films were deposited on Cu_2O films by a simple dipping method. The photovoltaic properties of the Cu_2O/Cu_xS heterojunction could be improved significantly by heat treatment in air. Although the efficiency of the cell is limited to 0.1% we believe that this system could be improved to obtain higher efficiency values.

Acknowledgements

This work was supported by a Research Grant (RG/88/p/01) from Natural Resources, Energy and Science Authority of Sri Lanka.

References

1. BERTOCCI, U. (1978) *J. Electrochem. Soc.* **125**, 1598.
2. BUBE, R.H. & FAHRENBRUCH, A.L. (1981) *Advances in Electronics and Electron Physics.* **56**, 163.
3. BURTON, L.C. & WINDAWI, H.M (1976) *J. Appl. Phy.* **47**, 4621.
4. DROZDOV, V.A., KURMASHEV, Sh.D. & RRACHER, A.L. (1965) *Soviet Physics–Doklady* **10**, 450.
5. GILL, W.D. & BUBE, R.H. (1970) *J. Appl. Phys.* **41**, 3731.
6. OSLEN, L.C., ADDIS, F.W. & MILLER, W. (1982) *Solar Cells* **7**, 247.
7. OLSEN, L.C., BOHARA, R.C. & URIC, M.W. (1979) *Appl. Phys. Lett.* **34**, 47.
8. ROTHWARF, A. & BOER, K.W. (1975) *Progress in solid state chemistry* **10**, 71.
9. SHIRLAND, F.A. & RAI–CHOUDHURY, P. (1978) *Rep. Prog. Physics* **41**, 1839.
10. SIRIPALA, W. & JAYAKODY, J.R.P. (1986) *Solar Energy Materials* **14**, 23.
11. TIN, C.C. & WEICHMAN, F.L. (1984) *Can. J. Phys.* **62**, 876.
12. TRIBUTSCH, H. (1984) *in studies in Inorganic Chemistry* **5**, 277.
13. TRIVICH, D., WANG, E.Y., KOMP, R.J. & KAHAR, A.S. (IEEE, New York, 1978) *13th IEEE Photovoltaic Spec. Conference, Washington D.C.* 1978 p. 174.
14. WEICHMAN, F.L. (1982) *Can. J. Phys.* **60**, 269.
15. WILHELM, S.M., TANIZAWA, V. CHANG–YI LIN & HARKERMAN, N. (1982) *Corr. Sci.* **22**, 791.