Ceylon Journal of Science: Physical Sciences, 4(1), 9-13 (1997)

SURFACE STATES AT p-$CuInSe_2$/AQUEOUS ELECTROLYTE INTERFACE

W. SIRIPALA,
Department of Physics, University of Kelaniya, Kelaniya, Sri Lanka.

ABSTRACT

Impedance measurements were used to evaluate the relative band edge positions of single crystal p-$CuInSe_2$ electrodes in aqueous 0.1M K_2SO_4 solution by measuring the extrapolated flat-band potentials, V_{fb}. We find that V_{fb} can be shifted by oxidation and reduction of the electrode surface and this observation was verified by chopped light current-potentialmeasurements. The surface state density distribution responsible for this shift was evaluated and found that it islocated at 0.43 eV above the valence band with a peak density of $3x10^{14}$ eV^{-1} cm^{-2} and it could be removed by electrochemical reduction.

1. INTRODUCTION

Copper Indium Diselenide is a promising semiconductor material for thin film solar cell applications [1]. In the most studied cell in this regard, $CdS/CuInSe_2$, it appears that the band line-up between the two semiconductors is a crucial parameter which determines the efficiency [2,3]. Three different band line up are illustrated schematically in fig. 1, as an example, to depict the effect of the band line-up on the open-circuit voltage, short circuit current and thereby the overall efficiency of the cell. Fig. 1(a) shows the exact matching of the band edges while fig. 1 (b) and (c) show the other two possibilities. In fig. 1(b) situation, one could expect a better short-circuit current because the photogenerated electrons in $CuInSe_2$ can be transeferred to CdS efficiently, compared to fig.1 (c). However, the open circuit voltage in fig. 1(b) situation is poor, compared to fig. 1 (c), because the Fermi level difference there is smaller. Therefore the band line up affects the open- circuit voltage, short circuit current and thereby the overall efficiency of the cell.

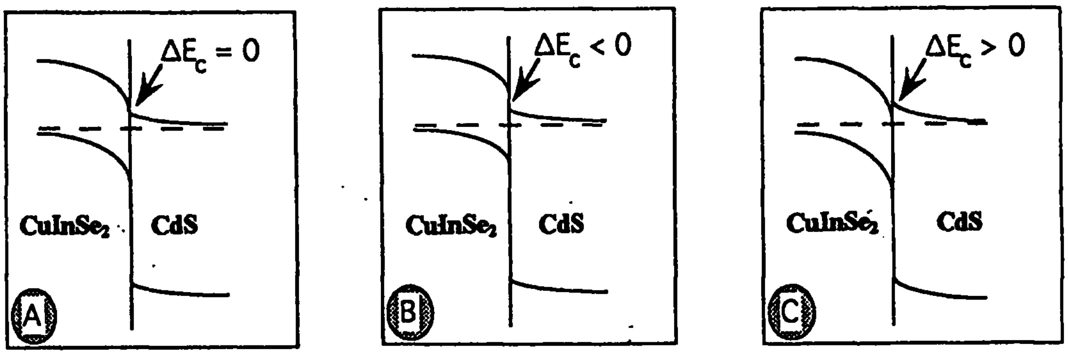

Fig.1. Schematic representation of three different band line-up positions of the $CuInSe_2$/CdS interface

Results from a number of studies on $CuInSe_2$ have pointed to the occurrence of significant shifts of the band edges of this material, depending on the electrolyte and the pretreatment given to the sample [4-8]. The existence of such shifts suggests the possibility of surface Fermi level engineering [9], via the ability to induce them and, especially, the possibility to control them. This is directly relevant for the effort to optimize all thin film solar cells based on $CuInSe_2$ as the absorber.

The evidence of the surface pretreatment that could shift the band edge positions in various aqueous electrolytes, as observed with impedance measurements, led us to investigate the observed shifts of the V_{fb} using another method of chopped light current-potential measurements. Also, a detailed analysis of the impedance data was used to evaluate the surface state density distribution at the $CuInSe_2$/electrolyte interface which caused the observed shifts in V_{fb}.

2. EXPERIMENTAL

Single crystals of $CuInSe_2$ were cut from a boule grown by the vertical Bridgman method. They were oriented crystallographically close to (112) or (110) planes. Back contact to the samples were made by evaporated Au or In-Ga eutectic. Samples were then encapsulated in an epoxy resin and the total exposed areas were between 0.02-0.15 cm^2. All the samples were etched in 1% Br_2/Ethylene Glycol solution for 2 minutes. We found that such an etching treatment removes, on the average, 300 nm/min of the exposed area of the sample. Electrolyte solutions were prepared using Millipore HQ deionized water and reagent grade chemicals, and they were deoxygenated in the electrochemical cell by argon bubbling during the experiments. Electrolyte used in this investigation was 0.1 M K_2SO_4.

The experimental set-up consisted of a three electrode electrochemical cell, a potentiostat (PAR173), a frequency generator (Waveteck model 188), a lock-in amplifier (Oretc-Brookdeal/9505) and a pc computer. We used a mercury sulfate electrode (MSE) as the reference electrode and a platinum wire as the counter electrode. The impedance of the semiconductor/electrolyte interface was determined by the analysis of its response to a 1μA alternating current signal at a frequency of 50 kHz [10,11]. This system allowed us to measure both the current and the interfacial capacitance as a function of the applied electrode potential. The scan speed was 10 mV/sec..

3. RESULTS AND DISCUSSION

The potential scan ranges were selected where reproducible current-voltage and capacitance -voltage characteristics could be obtained. Fig. 2 shows capacitance^{-2}-voltage (Mott-Schottky) plots for a p-$CuInSe_2$ sample in 0.1 M K_2SO_4 solution where the measurements were taken during a full cyclic scan started from a more anodic potential. Two distinct linear regions are very clearly seen, which when extrapolated lead to two different V_{fb} values, viz. -0.7 V Vs MSE and - 0.2 V Vs MSE.

As shown in fig.3 , the on-set of the photocurrent in the chopped light current-potential curves clearly indicates that there is a significant shift in the on-set potentials. Namely the photocurrent on-set has been shifted to more negative potential during the cathodic to anodic scan. Since the photocurrent on-set is closely related, in general, to the flatband potential, the observed shift could be directly associated with a shift in the flatband potentials.

The chemical interactions between the surface of a semiconductor and an electrolyte may change the surface chemistry and therefore in electrochemical studies those changes in the surface are observed by the shift in the band edge positions. It is clearly seen from both figures 2 and 3 that the oxidized surface has a more positive flatband potential and after reducing the surface it is shifted towards a more negative value.

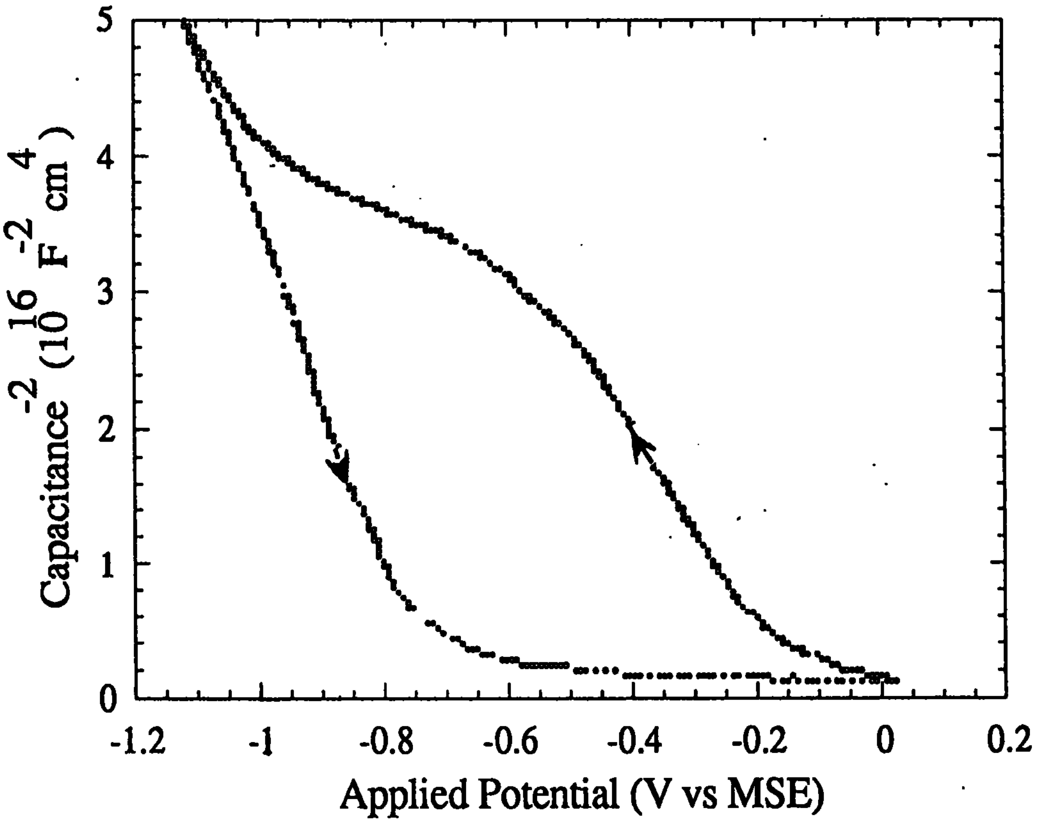

Fig. 2 Capacitance^{-2} Vs applied voltage curve for p-$CuInSe_2$ in 0.1M K_2SO_4. The directions of the scans are indicated by the arrows.

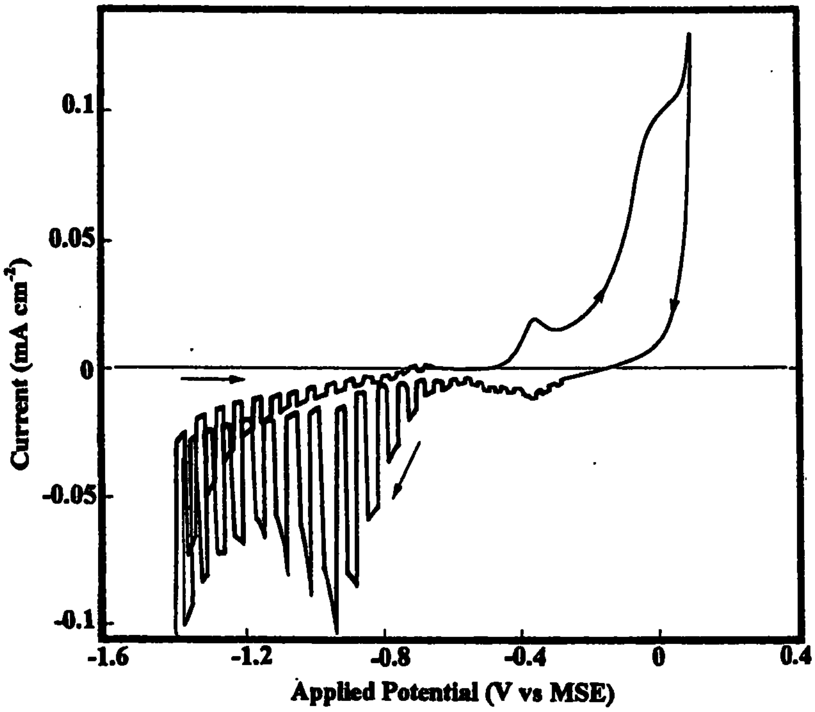

Fig.3 Current - potential scans under chopped light illumination in 0.1 M K_2SO_4

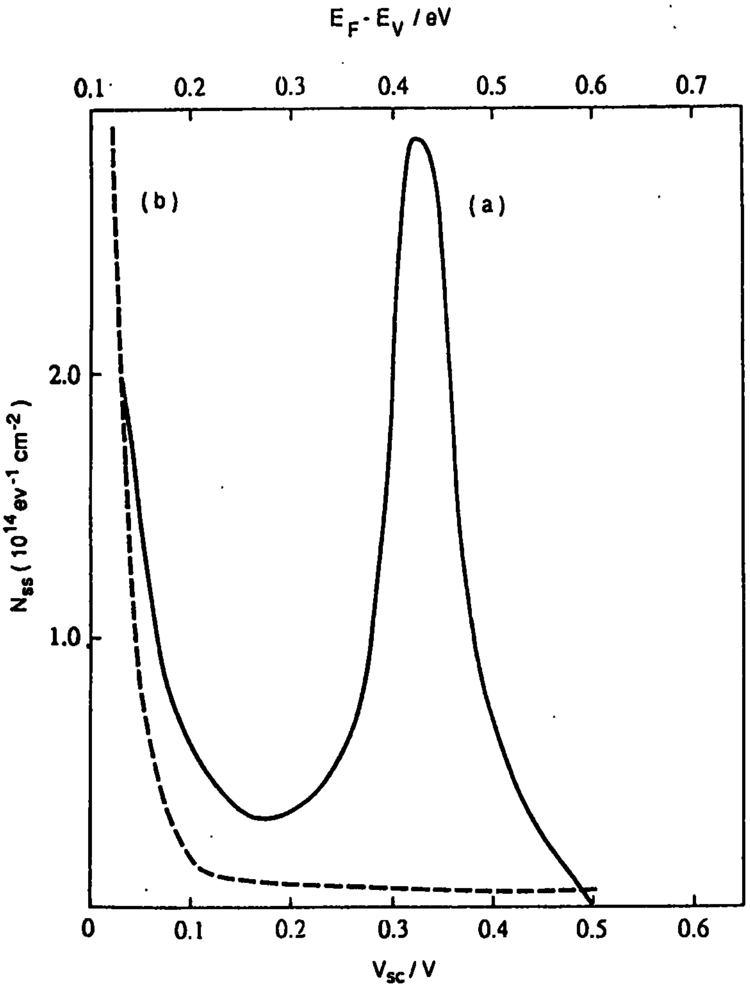

Fig.4 Variation of the surface state density (N_{ss}) with V_{sc} (lower scale) and with the energy within the gap (upper scale). (a) Cathodic scan from 0V to -1.1 V Vs MSE (b) Anodic scan from -1.1V to 0V Vs MSE.

The surface state density distribution within the energy gap of $CuInSe_2$, which is responsible for the charging and discharging of the surface, could be evaluated using the C^{-2} Vs V curves [10,11]. The key assumptions made in this evaluation are that the surface states are in thermal equilibrium with the bulk of the semiconductor material and their occupancy is determined by the Fermi level (E_F) at the surface, consequently, the band bending (V_{sc}) at the surface. As the surface is charged due to the charging/discharging of the surface states, the potential distribution at the interface is modified and as a result the relative band edge position is modified. Accordingly, as the surface is charged due to the applied potential, non-linear Mott-Schottky plots are obtained. This deviation is used to evaluate the distribution of surface states at the interface. Fig. 4 shows the density of surface states, N_{ss}Vs V_{sc} evaluated for a p-$CuInSe_2$ sample in 0.1 M K_2SO_4 adapting the same methodology explained in reference (10). Fig.4 (a) shows the density distribution for the scan from 0 V to -1.1 V Vs MSE while Fig.4(b) is that for the reverse scan. This was calculated from the C^{-2} Vs V curve for a full cyclic scan between 0 to -1.1V Vs MSE, for the same sample shown in fig.2. It is clearly seen that for the oxidized surface, fig. 4(a), the surface state density distribution is strongly localized in the energy gap and after the reduction it is completely removed, fig.4(b).

With the assumption of a 0.1 eV for the energy difference between the valence band edge (E_v) and the Fermi level (upper scale in fig.4), which is commonly used for this type of sample, we can estimate the peak position of the surface state density distribution to be at 0.43 eV above the valence band or located close to the middle of the band gap (E_g=1.0 eV). We believe that the surface modifications caused by the potential induced chemical reactions are responsible for the observed surface states distribution. Oxidation of p-CuInSe$_2$ samples in 0.1 M K$_2$SO$_4$ solution may induce surface states at the interface resulting in the observed surface state density distribution. However, these states are removed or deactivated by the reduction.

4. CONCLUSIONS

Impedance measurements and chopped light current-potential measurements reveal that the band edge position of p-CuInSe$_2$ in 0.1 M K$_2$SO$_4$ can be shifted by oxidizing and reducing the surface. We observed that surface state density distribution which is responsible for the observed shift in the band edges is strongly localized at 0.43 eV above the valence band and after reducing the surface it is completely removed.

ACKNOWLEDGEMENTS

Author wishes to acknowledge the financial assistance from EEC to conduct this research work at Labaratoire de Eelctrochomie, Paris, France. Drs. J.Vedel and D. Lincot at Labaratoire de Electrochime and Professor D.Cahen at Wiezman Institute of Science, Israel are gratefully acknowledged for their valuable contribution to this work.

REFERENCES

1. Rockett, A. and Birkmire R.W., *J. Appl. Phys.*, **70**, R81 (1991).
2. Turowski, M., Margaritondo, G., Kelly, M.K. and R.D.Tom Linso, R.D., *Phys. Review* **B, 31(2)**, 102 (1985).
3. Nelson A.J., Gebhard, S., Rockett, A., Colarita, E., Engelhart, M. and Hochst, H., *Phys. Review*, **B, 42,** 7518 (1990).
4. Cahen, D. and Mirovsky, Y., *J.Phys. Chem.*, **81**, 2818 (1985).
5. Cahen, D., Chen, Y.W., Noufi, R., Ahrenkiel, R., Matson, R., Tomkiewicz, M. and Shen, W., *Solar Cells*, **16**, 529 (1986).
6. Chen, Y.W., Cahen, D., Noufi, R.and Touner, J.A., *Solar cells*, **14**, 109 (1985).
7. Lincot, D., Meier, H.G., Kessler, J., Vedel, J., Dimmer, B.and Schock, H.W., *Solar Energy Materials*,**20**,67 (1990).
8. Siripala, W., Vedel, J., Lincot, D. and Cahen, D., *Appl. Phys.Lett.*,**62**,53 (1993).
9. Freouf, J.L., Warem, A.C., Kirchmer, P.D. and Woodal, J.M., *J. Vac.Sci.Tech.* **B9**,2355 (1991).
10. Lincot, D. and Vedel, J. *J.Electroanal. Chem.*,**175**, 207 (1984).
11. Frese, K.W. and Morrison, S.R., *J.Eelctrochem. Soc.*, **126**,1235 (1979).