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Thin film $CdZnS/CuInSe_2$ solar cells by spray pyrolysis

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Abstract. $Cd_{1-x}Zn_xS/CuInSe_2$ solar cells having efficiencies in the range of 2·3% were fabricated by spray pyrolysis. The best cell had the following parameters: $V_{oc} = 305$ mV, $J_{sc} = 32$ mA/cm², FF = 0·32 area = 0·4 cm² and efficiency = 3·149%. V_{oc} versus temperature measurements showed that the electron affinity difference was 0·22 eV. Forward dark current versus voltage curves were plotted and a possible current mechanism occurring in these cells has been proposed.

Keywords. $CuInSe_2$ solar cells; thin film solar cells; $CdZnS/CuInSe_2$; spray pyrolysis.

1. Introduction

$CuInSe_2$ is a I-III-VI_2 ternary chalcopyrite semiconductor which has recently excited considerable interest as a photovoltaic material. It has a direct band gap of 1·02 eV and falls in the optimum range for terrestrial photovoltaic applications (Kazmerski *et al* 1976, 1977). Owing to its high absorption coefficient, it requires at the most a few microns of thickness to make devices. Besides, inexpensive thin film deposition techniques can be used in the fabrication. $CuInSe_2$ when paired with CdS, has a compatible lattice structure with a lattice mismatch of only 1·2% and a favourable electron affinity difference (0·1 eV) (Tell *et al* 1972; Shay *et al* 1975; Chen and Mickelsen 1980). The $CdS/CuInSe_2$ solar cell has been modelled by Ireland *et al* (1979) and has been analysed as one of the highest efficiency photovoltaic heterojunctions available. A 11% thin film $CdZnS/CuInSe_2$ cell prepared by an elemental three-source evaporation has already been demonstrated by the Boeing Aerospace Co., Washington (Hermann *et al* 1984). The Boeing cells have been found to have excellent stability owing to the tetragonal structure of $CuInSe_2$ (Mickelsen and Chen 1982).

2. Experimental procedure

2.1 *$CuInSe_2$ films*

Aqueous solutions of cupric chloride, indium trichloride and seleno-urea were mixed together in the Cu:In:Se ratio of 1:1:4 and sprayed onto glass substrates heated to 300°C to obtain $CuInSe_2$ films about 1 μ thick. The films were characterized by x-ray diffraction, optical transmission spectra, transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and electrical measurements. The properties of these sprayed films have been reported elsewhere (Agnihotri *et al* 1983; Raja Ram *et al* 1985).

2.2 *Fabrication of cells*

A number of $Cd_{0.85}Zn_{0.15}S/CuInSe_2$ solar cells having efficiencies in the 2–3 % range were prepared by spray pyrolysis. Indium tin oxide films of high transmission and low sheet resistance (1–5 Ω/ □) were used as the substrates for the junctions.

The ITO substrates were placed on a hot plate, partially covered and heated to 350°C. A 1·5 μ thick layer of $Cd_{1-x}Zn_xS$ ($x = 0{\cdot}15$) was grown on the uncovered portion of the ITO by spraying a mixture of aqueous solutions of $CdCl_2$, $ZnCl_2$ and thiourea. Indium (5–10 %) in the form of $InCl_3$ solution was also added to reduce the resistivity of the CdZnS layer. The substrates were further covered and about 2 μ of $CuInSe_2$ were grown at 300°C. The junctions were then removed from the hot plate and fitted inside a vacuum coating chamber to deposit the gold contact on the $CuInSe_2$ back layer. Thus junctions of the type $ITO/CdZnS/CuInSe_2/Au$ were formed.

2.3 *Characterisation of the cells*

The cells were illuminated at 100 mW/cm^2 through the glass, ITO and CdZnS, and the I-V characteristics were plotted on an automatic I-V plotter. The values of V_{oc} versus

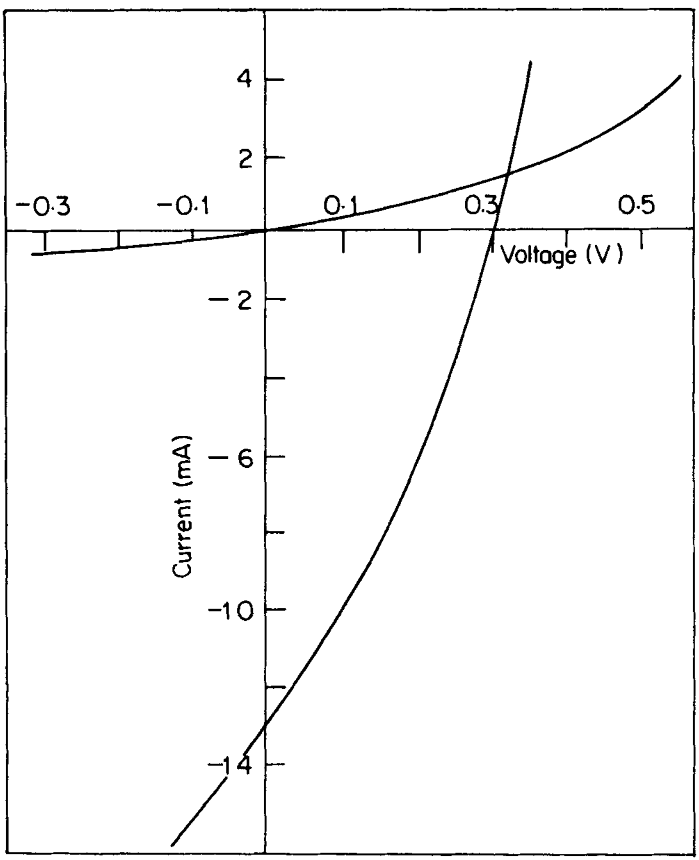

Figure 1. I-V characteristics of a $CdZnS/CuInSe_2$ solar cell illuminated at 100 mW/cm^2.

temperature and dark I-V plots at various temperatures were obtained by fitting the device in a copper cryostat cooled by liquid air.

3. Experimental results and discussion

Figure 1 shows the light I-V characteristics of the best $CdZnS/CuInSe_2$ cell. The parameters of the cell illuminated at $100\,mW/cm^2$ are: $V_{oc} = 305\,mV$, $J_{sc} = 32\,mA/cm^2$, FF = 0·324, area = $0{\cdot}40\,cm^2$ and efficiency $\eta = 3{\cdot}149\%$.

In general the cells had high short circuit currents, but low open circuit voltages, small fill factors and consequently low efficiencies.

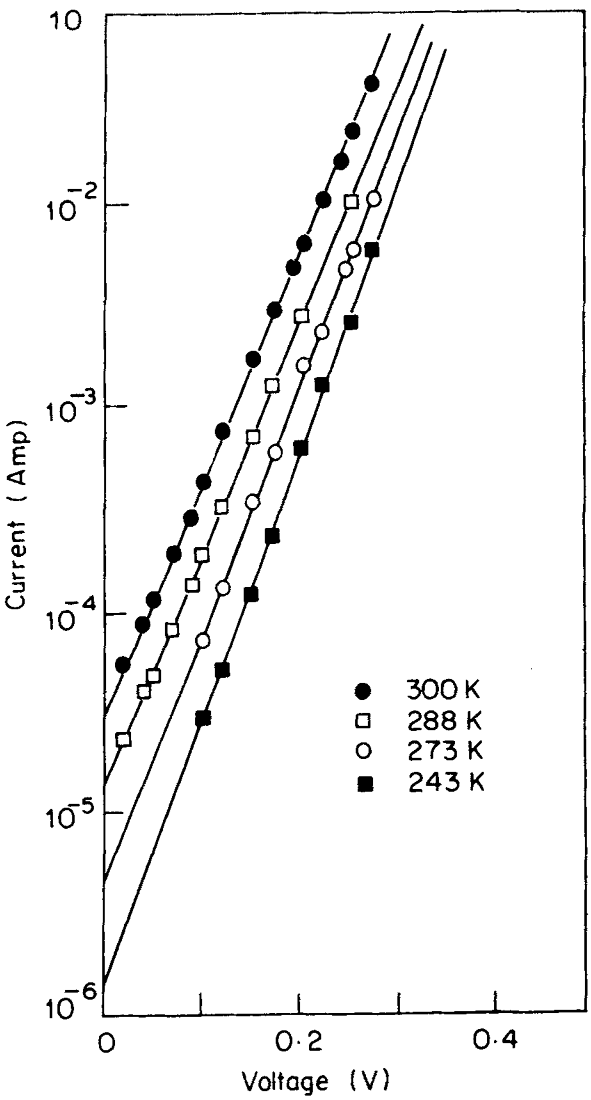

Figure 2. Dark current vs voltage at various temperatures for $CdZnS/CuInSe_2$ cell.

If the cell is dominated by interface recombination, the current through the junction is of the form (Kazmerski *et al* 1978):

$$J = J_0 \exp(qV/nkT)$$

where

$$J_0 = J_{00} \exp\left\{-\frac{(E_{g1} - \Delta\psi)}{nkT}\right\},$$

where q is the charge of an electron, V is the applied voltage, n is the diode factor, E_{g1} is the band gap of $CuInSe_2$, $\Delta\psi$ is the electron affinity difference between the $CuInSe_2$ and CdZnS.

The diode factor n of the best cell was about 1·5, confirming that interface recombination is the dominant mechanism in these junctions. Figure 2 shows the dark I-V plots for the best cell for various device temperatures. The intercept on the current axis gives the ($J_0 \times$ area) value for each temperature. Figure 3 shows the J_0 versus $1/nkT$ plot whose slope gives the diffusion voltage in the dark. Here it is 0·63 V. For a planar diode, the open circuit voltage V_{oc} can be written as:

$$qV_{oc} = E_{g1} - \Delta\psi + nkT \cdot \ln\left(\frac{J_{sc}}{qN_{C2}S_1}\right) - \delta_1 - \delta_2,$$

where δ_1 and δ_2 are the energy differences between the fermi level and the valence and conduction band edges as shown in figure 5. The V_{oc} versus T plot is shown in figure 4. The intercept on the V_{oc} axis gives the value of $E_{g1} - \Delta\psi = 0{\cdot}82$ eV. Thus the value of $\Delta\psi$ is 0·22 eV assuming that the band gap of sprayed $CuInSe_2$ is 1·04 eV.

From the above results the energy band diagram has been drawn for these $CdZnS/CuInSe_2$ cells. This is shown in figure 5.

The resistivities of the $CuInSe_2$ and CdZnS layers forming the junction are about 100 Ω cm and 50 Ω cm respectively. The values for the carrier concentrations p and n_e given in the figure are typical values obtained from Hall and thermoelectric measurements conducted on the films.

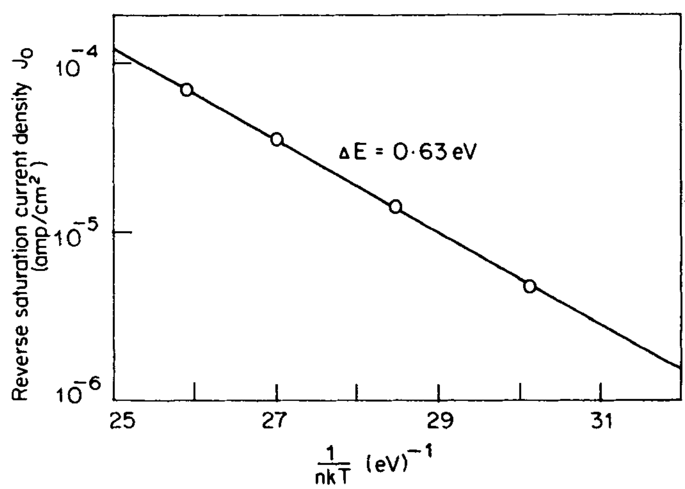

Figure 3. J_0 vs $(nkT)^{-1}$ for the cell.

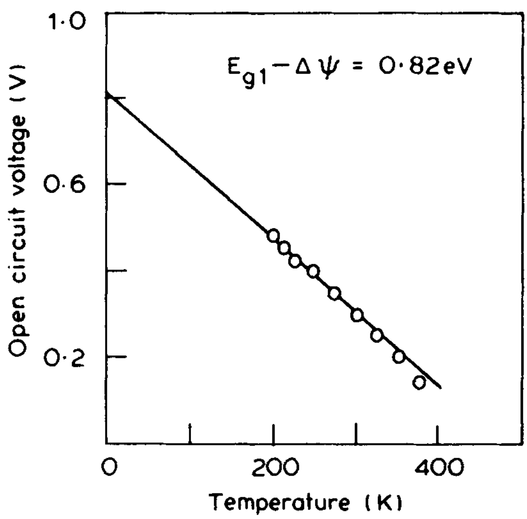

Figure 4. V_{oc} vs temperature for the cell.

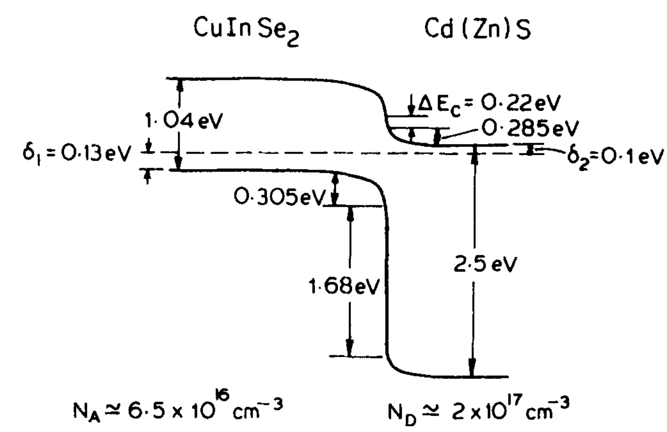

Figure 5. Proposed energy band diagram for the $CuInSe_2$/CdZnS junction.

The proposed band diagram explains some of the properties like low V_{oc} and efficiency of the cells. The V_{oc} is low due to: (i) the spreading of the junction field region into the CdZnS because the condition $n_e \gg p$ does not hold. A part of the diffusion voltage appears across the CdZnS and only the remaining part contributes to the V_{oc}. (ii) The high values of δ_1 and δ_2 which can be reduced only if the resistivity of the CdZnS is further decreased without compromising the film quality.

Another important factor which causes a reduction in both V_{oc} and the fillfactor is the low shunt resistance. The shunt resistance is small due perhaps to the recombination along the grains and the defects which are in large numbers in sprayed films. The low values of V_{oc} and FF thus result in low efficiencies of the cells.

4. Conclusions

$CdZnS/CuInSe_2$ solar cells with efficiencies around 3% were prepared by spray pyrolysis. The efficiency can be increased by reducing the resistivity of the CdZnS layers and by improving the quality of the sprayed $CuInSe_2$ and CdZnS films. We are grateful to DRDO, Ministry of Defence, Government of India for financial support.

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