

Photoelectrochemical Behavior of $\text{CuIn}_{0.4}\text{Ga}_{0.6}\text{Se}_2$ thin Films Deposited by Pulse Plating

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ABSTRACT

Thin films of $\text{CuIn}_{0.4}\text{Ga}_{0.6}\text{Se}_2$ (CIGS) were pulse electrodeposited at a duty cycle of 50 % on indium tin oxide coated glass substrates. The films were characterized by structural, electrical and photoelectrochemical properties. XRD studies indicate the presence of single phase CIGS. The electrical resistivity of all the samples are calculated by using Van der Pauw technique and found to be 0.45 ohm cm. Photoelectrochemical cell studies indicated a solar to electrical conversion efficiency of 14.78 % after photoetching for 80 s. Mott Schottky study indicated the film to exhibit p-type behavior.

Keywords: CIGS, Photoelectrochemical, Pulse deposition, P-type, Thin films.

I. INTRODUCTION

The most promising material for low cost and high efficiency thin film solar cell application is $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS). The salient feature of this material is its superior optical properties with a high absorption coefficient ($\alpha \sim 10^5 \text{ cm}^{-1}$), long-term stability and high tolerance to radiation. Further, the band gap of CIGS can be varied by introducing indium to partially replace gallium. This feature enables to manipulate the optical absorption [1]. Various methods that were employed for preparing CIGS absorber layers include vacuum co-evaporation [2], sputtering [3], pulsed laser deposition [4], ink-printing [5] and electrochemical deposition [6]. In this work, the pulse electrodeposition technique was employed to deposit CIGS thin films.

II. EXPERIMENTAL METHODS

$\text{CuIn}_{0.4}\text{Ga}_{0.6}\text{Se}_2$ films were pulse electrodeposited on indium tin oxide coated glass substrates at 50 % duty cycle at room temperature. The precursors used were 20 mM SeO_2 , 40 mM CuCl_2 , 60mM InCl_3 and 50 mM GaCl_3 . All chemicals were of AR quality (99.99%). The deposition potential was maintained at -0.8V (SCE). The pH was maintained at 1.5 by HCl. A microprocessor controlled pulse plating unit was used. Thickness of the films measured by Mitutoyo surface profilometer was 950 nm. The films were characterized by Xpert analytical x-ray diffraction unit with Cu $\text{K}\alpha$ radiation. Photoelectrochemical cell studies were made using a 250 W tungsten halogen lamp and a water filter to cut off IR. Polysulphide (1M NaOH, 1M Na_2S , 1M S) was used as the redox electrolyte. The intensity of light falling on the electrode was measured by a CEL suryamapi.

III. RESULTS AND DISCUSSION

Microstructural parameters were estimated by studying the x-ray diffractograms of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ films.

Fig.1 shows the x-ray diffraction patterns of the films. The XRD pattern indicates the prominent peaks corresponding to (112), (220)/(204), (312)/(116). These are characteristic of the chalcopyrite phase. No other phases were observed in the x-ray diffractograms indicating the formation of single phase material. The lattice parameters were calculated using the following relation [7]

$$1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2 \dots\dots\dots(1)$$

Where, ‘a’ and ‘c’ are the lattice parameters, “d” is the lattice spacing. The lattice parameter values are

a = 0.5693 nm and c = 1.133 nm. The grain size of the films have been calculated using Scherrer's formula [8],

$$D = 0.94\lambda / \beta \cos\theta \dots\dots\dots(2)$$

where λ is the wavelength of X-ray used, β the full-width half-maximum (FWHM) and θ the Bragg angle. The grain size was 49 nm. The grain size is smaller than those obtained with sputtered CIGS films [9].The dislocation density δ , was evaluated using the following formula [10]

$$\delta = 1/D^2 \dots\dots\dots(3)$$

Composition of the films was estimated by recording the EDS spectrum of the films deposited of different composition. Fig.2 shows the EDS spectrum of $CuIn_{0.4}Ga_{0.6}Se_2$ films deposited at 50 % duty cycle. The film composition was Cu = 22.20 %, In = 9.00 %, Ga = 14.00 %, Se = 53.80 %, Cu/(Ga +In) ratio = 1.01. Based on the defect chemistry model of ternary compounds [11], compositional deviations of the $CuIn_{1-x}Ga_xSe_2$ films can be expressed by non-stoichiometry parameter ($\Delta y = [2Se/\{Cu + 3(Ga + In)\}] - 1$). The parameter Δy is related to the electronic defects. For $\Delta y > 0$, the film has a p-type conductivity and it has an n-type conductivity for $\Delta y < 0$. In this study the value of $\Delta y = 0.17$, which is greater than zero, hence according to the above model, these films exhibit p-type conductivity.

The Hall Van der Pauw technique was used to determine theroom temperature transport parameters by providing gold ohmic contact. The room temperature resitivity was 0.45 ohm cm, room temperature mobility was $26.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and carrier density was $5.33 \times 10^{17} \text{ cm}^{-3}$. The resistivity and carrier concentration values are quite comparable those obtained with RF sputtered CIGS films [9].

The Photoelectrochemical cells (PEC) cells using the as deposited films exhibited low photocurrent and photovoltage, hence, in order to increase the photo output, the films of different composition were post heated in argon atmosphere at different temperatures in the range of 450 - 550°C for 15 min. The intensity of the light falling on the films deposited at different duty cycles was kept constant at 60 mW cm^{-2} . Fig. 3 exhibits the load characteristics of $CuIn_{0.4}Ga_{0.6}Se_2$ films deposited at 50 % duty cycle and post heat treated at different temperatures. From the figure, it is observed that the PEC output parameters, viz., open circuit voltage and short circuit current were found to increase for the electrodes heat-treated upto a temperature of 525°C. Photoelectrodes heat-treated at temperatures greater than this value exhibited lower open circuit voltage and short circuit current due to the reduction in thickness of the films as well as the slight change in stoichiometry. The photovoltaic parameters are $V_{oc} = 0.57 \text{ V}$, $J_{sc} = 11.55 \text{ mA cm}^{-2}$, ff of 0.68, η of 7.46 %. Both V_{oc} and J_{sc} increased with increase of intensity. Beyond 80 mW cm^{-2} illumination, V_{oc} was found to saturate as is commonly observed in the case of photovoltaic cells and PEC cells, J_{sc} is found to linearly increase with intensity of illumination.

Photoetching was done by shorting the photoelectrodes and the graphite counter electrode under an illumination of 100 mW cm^{-2} in 1 : 100 HNO_3 for different durations in the range 0 – 100s. Both photocurrent and photovoltage are found to increase up to 80s photoetch, beyond which they begin to decrease. This is illustrated

in Fig.4 for the $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$ films deposited at 50 % duty cycle after post heat treatment. The decrease of the photocurrent and photovoltage after 80s photoetch is attributable to separation of grain boundaries due to prolonged photoetching [12]. The power output characteristics (Fig.5) after 80s photoetching indicates a V_{oc} of 0.70V, J_{sc} of 19.0 mA cm^{-2} , ff of 0.71 and η of 15.74 %, for 60 mW cm^{-2} illumination.

The charge distribution at the semiconductor and electrolyte interface is often determined by measuring the capacitance of the space- charge layer C_{sc} as a function of the electrode potential V . The Mott-Schottky relationship expresses the potential dependence of C_{sc} of a semiconductor electrode under depletion conditions

$$1/C_{sc}^2 = [2/eN_A \epsilon \epsilon_0][(V - V_{fb}) - kT/e] \dots \dots \dots (4)$$

where, C_{sc} is the space charge capacitance; V represents the applied potential; V_{fb} is the flat-band voltage; N_A is the concentration of acceptors, N_A can be determined from the slope of the experimental $1/C_{sc}^2$ versus V plots, while V_{fb} comes from the extrapolation for $1/C_{sc}^2 = 0$. The validity of the Mott-Schottky analysis is based on the assumption that the capacitance of the space charge layer is much less than that of the Helmholtz layer. When the measured frequency is high enough ($> 1 \text{ kHz}$), the contribution of Helmholtz capacitance to the measured electrode capacitance is negligible. Thus, the capacitance of the semiconductor/ electrolyte interface mainly expresses the capacitance of the space charge layer of the semiconductor. Mott-Schottky plot of the CIGS films of different composition with $1\text{M Na}_2(\text{SO}_4)_2$ blocking electrolyte was studied, the AC frequency was 10 kHz . Linear plot was obtained. The nature of the plot with positive slope indicates p-type behavior. V_{fb} of 0.80V (SCE) (Fig.6). The value of carrier density from the slope of the plot yields values of $1.2 \times 10^{17} \text{ cm}^{-3}$

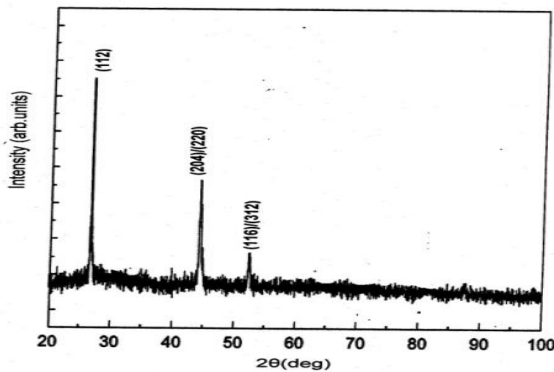


Fig.1- X-ray diffraction pattern of CIGS

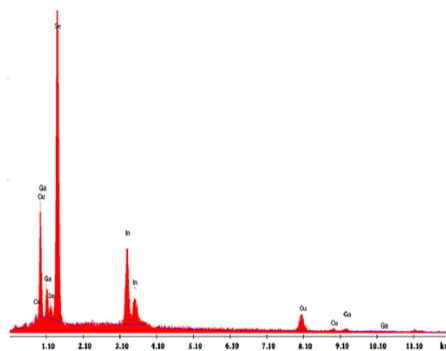


Fig.2-EDAX spectrum of CIGS

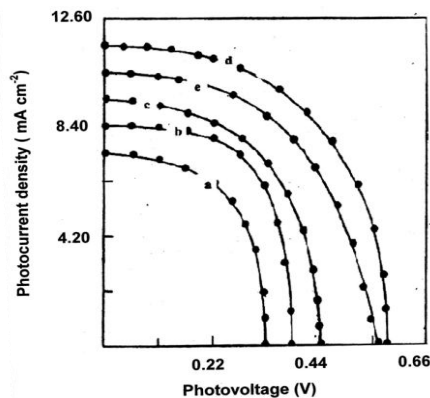
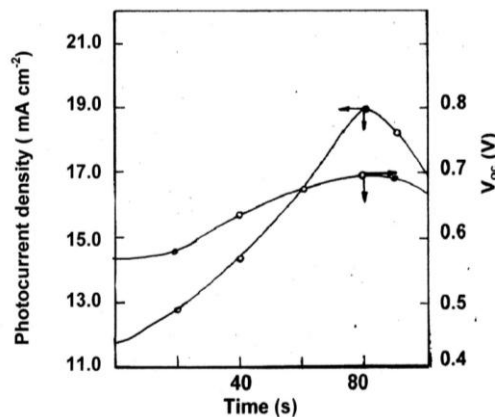


Fig.3- Load Characteristics of CIGS



Fif.4-Photo etching after heat treatment

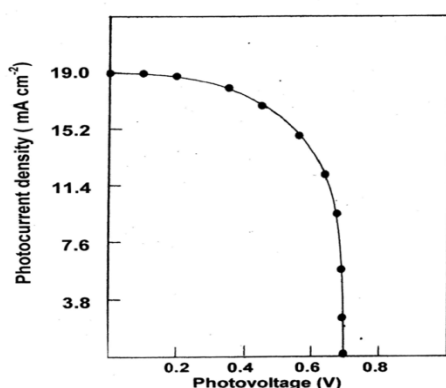


Fig.5-Photocurrent-photovoltage characteristics of CIGS

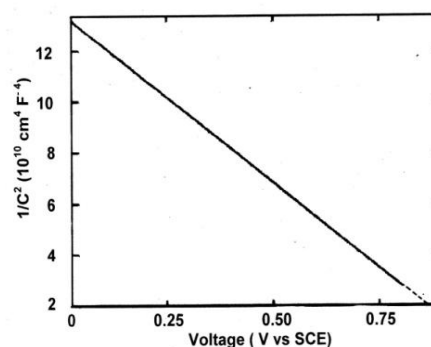


Fig.6- Mott-Schottky plot of CIGS

IV. CONCLUSION

CuIn_{0.5}Ga_{0.5}Se₂ thin films were deposited by the pulse electrodeposition technique at 50 % duty cycle. The films were polycrystalline and exhibited a chalcopyrite structure with (112) preferred orientation. The grain size was 49 nm. The room temperature electrical resistivity of the films was 0.45 ohm cm. Photoelectrochemical cells exhibited a solar to electrical conversion efficiency of 14.78 % after photoetching.

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