Photoelectrochemical investigation on spray deposited n - CdIn_2S_4 thin films

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Abstract. Polycrystalline thin films of n - CdIn_2S_4 have been spray deposited onto amorphous and fluorine-doped tin oxide (FTO) coated glass substrates at the optimized substrate temperature of 380°C . The films were characterized by X-ray diffraction (XRD) and optical absorption studies. XRD studies revealed that the films were polycrystalline with spinel cubic structure. The optical absorption studies showed the band gap energy to be 2.14 eV . Photoelectrochemical (PEC) investigations were carried out using cell configuration n - $\text{CdIn}_2\text{S}_4/1\text{ M NaOH} + 1\text{ M Na}_2\text{S} + 1\text{ M S/C}$. Using Butler model, the optical band gap and minority carrier diffusion length (L_p) were found to be 2.22 eV and $0.07\text{ }\mu\text{m}$, respectively. Gartner's model was used to calculate the minority carrier diffusion length and the donor concentration (N_D) for CdIn_2S_4 films at three different wavelengths. N_D was found to be of the order of 10^{16} cm^{-3} .

Keywords. Spray pyrolysis; thin films; Cd chalcogenides; PEC cells.

1. Introduction

For the last couple of decades, interest in the use of photoelectrochemical (PEC) solar cells led to large amount of research, in the search for thin film polycrystalline materials with acceptable efficiency; sometimes approaching to that of single crystals. A vast amount of literature is available on the preparation and characterization of semiconductor chalcogenide electrodes.

Cadmium indium sulphide (CdIn_2S_4) is a photoconductive compound semiconductor having spinel structure (Kambas *et al* 1985) of the type $\text{A}^{\text{II}}\text{B}^{\text{III}}\text{C}^{\text{VI}}$ to which great attention has been devoted in the last few years. At room temperature, the values of the direct gap ranged from 2.10 to 2.42 eV and for indirect gap it varied from 2.00 to 2.20 eV (Anedda and Fortin 1979). Various studies (Anedda and Fortin 1979; Epps and Becker 1982) have confirmed CdIn_2S_4 single crystals to be photoactive. Photoelectrochemical studies of spinel CdIn_2S_4 single crystals in various electrolytes were reported by Epps and Becker (1982). A 1.2% light to electrical conversion efficiency was shown for the iron hexagon ($\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$) system.

In the present investigation, an attempt is made, for the first time, to investigate the behaviour of spray deposited n - CdIn_2S_4 thin film photoelectrode by studying the properties of n - CdIn_2S_4 thin film/polysulphide junction.

2. Experimental

2.1 Preparation of CdIn_2S_4 thin films

CdIn_2S_4 thin films were deposited onto amorphous and fluorine-doped tin oxide (FTO) coated glass substrates by

taking equimolar solution of cadmium chloride (CdCl_2), indium trichloride (InCl_3) and thiourea [$\text{CS}(\text{NH}_2)_2$] in appropriate volumes to obtain Cd : In : S ratio as $1 : 2 : 4$, respectively. The films were prepared at the optimized 50 mM concentration of a mixed solution and a substrate temperature of 380°C . These optimized conditions of solution concentration and substrate temperature were obtained by choosing the films having relatively higher photovoltaic activity when used in PEC cells. The films were deposited by spraying 20 cm^3 solution at the rate of $3\text{ cm}^3\text{ min}^{-1}$. Air was used to atomize the spray. The deposited films were bright yellow in colour having $1.11\text{ }\mu\text{m}$ thickness.

The structural characterization of film was carried out by analyzing the XRD pattern, obtained using a Philips X-ray diffractometer model PW-1710 ($\lambda = 0.15405\text{ nm}$ for Cu-K α). Optical absorption studies were carried out using a UV-VIS-NIR spectrophotometer (Hitachi Model 330, Japan) in the wavelength range $350\text{--}850\text{ nm}$.

2.2 Photoelectrochemical (PEC) characterization of CdIn_2S_4 thin films

The PEC cell was fabricated by using CdIn_2S_4 thin film as active photoelectrode, polysulphide ($1\text{ M NaOH} + 1\text{ M Na}_2\text{S} + 1\text{ M S}$) solution as an electrolyte and carbon as a counter electrode. The distance between photoelectrode and counter electrode was 0.2 cm . The cell was illuminated by 500 W tungsten filament lamp. The water lens was interposed between the lamp and the cell to avoid heating of the cell. The type of conductivity exhibited by the film was determined by noting the polarity of the photovoltage developed in PEC cell under illumination. Spectral response studies were conducted for CdIn_2S_4 thin

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film electrode/polysulphide PEC system in the wavelength range 350–850 nm.

3. Results and discussion

3.1 X-ray diffraction (XRD) studies

The as-grown films were characterized by XRD technique with Cu-K α radiation with Ni filter. The XRD patterns obtained for the films grown on bare microslide glass plates were studied in 2θ range 10–100°. The XRD pattern show that the films are polycrystalline (figure 1). Table 1 compares the d values of the typical film calculated from the X-ray diffractogram with the standard d values of CdIn₂S₄ (JCPDS diffraction data file Nos. 31-229 and 27-60). A matching of the observed and standard d values of n -CdIn₂S₄ films shows that the CdIn₂S₄ films are of spinel cubic structure. The calculated standard values of lattice constant are found to be 11.822 Å agreeing well with the standard values.

3.2 Optical absorption studies

Optical absorption studies of CdIn₂S₄ films deposited on pre-cleaned glass plates were carried out in the wavelength range 350–850 nm at room temperature. For allowed indirect band gap electronic transition, the absorption coefficient, ' α ' is given by (Pankov 1971; Chandra 1985)

$$\alpha = \frac{A}{hv} (hv - E_g)^2, \quad (1)$$

where A is constant, v the incident photon frequency, h the

Figure 1. X-ray diffractogram of sprayed CdIn₂S₄ thin film.

Plank's constant and E_g the band gap. The plot of $(\alpha hv)^{1/2}$ vs hv (figure 2) is linear indicating that the nature of the optical transition in semiconducting CdIn₂S₄ is indirect. The intercept on the energy axis at $\alpha = 0$ yields E_g to be 2.15 eV which is very near to the band gap value given in the literature (Radauston *et al* 1972; Fujita and Okada 1974).

3.3 Spectral response studies

Spectral response studies were conducted for CdIn₂S₄ thin film electrode/polysulphide PEC system in the wavelength range 350–850 nm under monochromatic illuminations by measuring the short circuit photocurrent density (I_{sc}) as a function of wavelength as shown in figure 3. It can be seen that I_{sc} increases with increase in wavelength, attains the maximum value of 500 nm and then decreases for further increase in wavelength. The lower photocurrent on the shorter wavelength side may be due to the absorption of light in the electrolyte and the larger amount of surface recombination of the photogenerated minority carriers. However, the smaller photocurrent of longer wavelength is attributed to lower absorption of the light at the photoanode used. The quantum efficiency, Q_F is given by (Chandra and Pandey 1982)

$$Q_F = \frac{\text{Number of photoelectrons generated/area}}{\text{Number of incident photons/area}}, \quad (2)$$

and is calculated from the equation (Das and Damodare 1998)

$$Q_F = \frac{I_{sc} (A/cm^2) \times hv (eV)}{q \times \text{intensity of light (W/cm}^2\text{)}}. \quad (3)$$

Figure 4 shows the variation of Q_F with photon energy. Peak quantum efficiency of 0.62 is observed at 475 nm. No corrections were made for solution absorption.

Table 1. Comparison of XRD data of CdIn₂S₄ thin films with ASTM data.

Sl. no.	Standard ' d ' (Å)	Observed ' d ' (Å)	hkl planes
1	6.260	5.960	111
2	3.834	3.817	220
3	3.131	3.185	222
4	3.052	3.061	320
5	2.712	2.685	400
6	2.213	2.202	422
7	2.087	2.059	511
8	1.911	1.895	440
9	1.635	1.633	622
10	1.565	1.546	444
11	1.519	1.493	551, 711
12	1.412	1.463	731
13	1.355	1.340	800
14	1.244	1.241	662
15	1.212	1.202	840

Under the assumption of Gartner's model and for the case of *n*-type semiconductor, the photocurrent is given by (Butler 1977)

$$I_{ph} = -qh\nu \left\{ 1 - \frac{e^{-\alpha W}}{1 + \alpha L_p} \right\}, \quad (4)$$

where $h\nu$ is the photon flux, α the absorption coefficient, L_p the hole diffusion length, q the electronic charge and W the width of the depletion layer which is given by

$$W = W_0(V - V_{fb})^{1/2}, \quad (5)$$

and

$$W_0 = \left\{ \frac{2\epsilon\epsilon_0}{qN_D} \right\}^{1/2}, \quad (6)$$

where V_{fb} is the flat band potential, $(V - V_{fb})$ the band bending, ϵ and ϵ_0 are the dielectric constants of semiconductor and vacuum, respectively and N_D donor concentration.

Substituting the value of W in (4) and if $L_p \ll 1$ and $\alpha W_0(V - V_{fb})^{1/2}$, the relation between the applied reverse bias potential and photocurrent becomes

$$(V - V_{fb}) \approx \left(\frac{I_{ph}}{\alpha W_0 q h \nu} \right)^2. \quad (7)$$

The band gap of a material is determined by using the following relation (Das and Damodare 1998)

$$(Q_F h \nu)^2 = (L_p + W)^2 A^2 (h \nu - E_g), \quad (8)$$

where A is a constant and Q_F the quantum efficiency. The

Figure 2. Plot of $(\alpha h \nu)^{1/2}$ vs $h \nu$ for sprayed CdIn₂S₄ thin film.

Figure 3. Variation of photocurrent with wavelength for a *n*-CdIn₂S₄/1 M NaOH + 1 M Na₂S + 1 M S/C PEC cell.

Figure 4. Variation of quantum efficiency vs photon energy for *n*-CdIn₂S₄/1 M NaOH + 1 M Na₂S + 1 M S/C PEC cell.

plot of $(Q_F h\nu)^2$ vs $h\nu$ allows E_g to be obtained. Figure 5 shows the variation of $(Q_F h\nu)^2$ vs $h\nu$. Extrapolation of linear portion of this curve gives the value of E_g equal to 2.22 eV. The value of E_g obtained is in good agreement with others (Radauston *et al* 1972; Fujita and Okada 1974) and our results obtained from optical measurements.

In the region of weak absorption, such that $L_p \ll 1$ and $\alpha W < 1$ (Ramprakash *et al* 1988), the following relation is valid.

$$Q_F = \alpha L_p. \quad (9)$$

Hence

$$(Q_F)^{-1} = (\alpha L_p)^{-1}. \quad (10)$$

From the plot of $(Q_F)^{-1}$ vs $(\alpha)^{-1}$ (figure 6), L_p is obtained from the inverse of the slope and is found to be 0.07 μm .

Equation (7) is used to estimate the value of flat band potential of the PEC cell. A linear relationship between the square of the photocurrent and applied voltage was observed and is shown in figure 7 for three different wavelengths. The value of flat band potential was obtained by extrapolating the straight lines to zero photocurrent and was equal to 0.13 V/SCE for 450, 475 and 500 nm incident wavelengths.

According to Kennedy and Frese (1976), Gartner's theory of Schottky barrier model to the semiconductor electrolyte interface also provides, with some limitations,

Figure 5. Plot of $(Q_F h\nu)^2$ vs $h\nu$ for sprayed CdIn_2S_4 thin film.

Figure 6. Plot of Q_F^{-1} vs α^{-1} for $n\text{-CdIn}_2\text{S}_4$ thin film.

Figure 7. Plot of square of photocurrent vs applied potential for three different wavelengths.

Figure 8. Plot of $\ln(1 - Q_F)$ vs $(V - V_{fb})^{1/2}$ for three different wavelengths.

a direct determination of donor density and diffusion length

$$\ln(1 - Q_F) = -\left(\frac{2\epsilon\epsilon_0}{qN_D}\right)^{1/2} (V - V_{fb})^{1/2} - \ln(1 + \alpha L_p). \quad (11)$$

According to (11), plot of $\ln(1 - Q_F)$ vs $(V - V_{fb})^{1/2}$ should be linear with slope equal to $-[(2\epsilon\epsilon_0)/(qN_D)]^{1/2}$ and intercept of $-\ln(1 + \alpha L_p)$ from which N_D and L_p can be obtained. Figure 8 shows plot of $\ln(1 - Q_F)$ vs $(V - V_{fb})^{1/2}$ for wavelengths 450, 475 and 500 nm. Using the value of ' α ' obtained from optical absorption measurement and $\epsilon = 6.6$ (Fujita and Okada 1974), the value of L_p and N_D were calculated. The analysis of figure 8 yields carrier concentration N_D to be about 18.9×10^{16} , 2.37×10^{16} and $1.92 \times 10^{16} \text{ cm}^{-3}$ and hole diffusion length

as 0.26, 0.55 and 0.22 μm for incident wavelengths of 450, 475 and 500 nm, respectively. The values of diffusion length appear reasonable although, as yet, there is no independent measurement of this quantity.

4. Conclusions

Gartner's model is useful in estimating different physical parameters of the photoelectrode of a PEC cell. The value of the V_{fb} determined from the photoresponse is -130 mV/SCE . The values of carrier concentration are 18.9×10^{16} , 2.37×10^{16} and $1.92 \times 10^{16} \text{ cm}^{-3}$ whereas hole diffusion lengths are 0.26, 0.55 and 0.22 μm for incident wavelength of 450, 475 and 500 nm respectively.

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References

- Anedda A and Fortin E 1979 *J. Phys. Chem. Solids* **40** 653
- Butler M A 1977 *J. Appl. Phys.* **48** 1914
- Chandra S 1985 *Photoelectrochemical solar cells* (New York: Gordon and Breach Science Publishers) vol. 5
- Chandra S and Pandey R K 1982 *Phys. Status Solidi (a)* **12** 415
- Das V D and Damodare L 1998 *Mater. Chem. Phys.* **56** 116
- Epps G F and Becker R S 1982 *J. Electrochem. Soc.* **129** 2628
- Fujita H and Okada Y 1974 *Jap. J. Appl. Phys.* **13** 1823
- JCPDS diffraction data file no. 31-229
- JCPDS diffraction data file no. 27-60
- Kambas K, Anagnostopoulos A, Ves S, Ploss B and Spyridelise J 1985 *Phys. Status Solidi (b)* **127** 201
- Kennedy H and Frese K W 1976 *J. Electrochem. Soc.* **26** 1683
- Pankov J I 1971 *Optical processes in semiconductors* (ed.) N Holonyak Jr (NJ: Solid State Physical Electronic Series, Prentice Hall) p. 34
- Radauston S I, Molodyan I P, Syrdy N N, Fezievan V E and Shipitka M A 1972 *Phys. Status Solidi (b)* **49** K175
- Ramprakash Y, Subramanian V, Krishnakumar R, Laxmanan A S and Venkatesen V K 1988 *J. Power Source* **24** 329