To study effect of temperature on ultra thin films of CdSe by electro deposition technique on mirror glass substrate in non-aqueous bath solution

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ABSTRACT

CdSe ultra thin films were deposited by using DC electro deposition technique on mirror glass substrate in non-aqueous bath. The preparative parameters were optimized to get good quality CdSe thin films. X-ray diffraction analysis of the deposited films showed the presence of polycrystalline nature with Hexagonal phase. Temperature effect also observed that the deposition potential decreases with increase in the bath temperature. The surface morphology studies by SEM show that the deposited film is well adherent & grains are uniformly distributed over the surface of substrate. Optical absorption study showed that CdSe films were of direct band gap type semiconductor with band gap energy of 1.70 eV

Key words: DC Electro deposition, XRD, SEM, Optical, Mirror Glass etc.

INTRODUCTION

Electro deposition is more than 150 years old thin film preparation technique which has largely been used to deposit metal films¹. In addition, during the last twenty five years electro deposition has been more intensively studied in preparing compound semiconductors in comparison with other techniques.

In literature, most of the CdSe films electro deposited from aqueous Acidic baths usually contain large concentration of elemental selenium (Pandey et al 1991, Gutierrez & Ortega (1989) that weakly crystallizes & the micrographs showed a cauliflower like appearance, which remained unchanged after annealing but very few workers (Baranski & Fawcett 1980, Baranski et al 1983, Skyllas – Kazacos & miller 1980) deposited these films from non- aqueous baths. Compared to water, non aqueous solvents offer an alternative process with some advantages.

In view of this, the present study deals with preparation of CdSe thin films by DC electro deposition method on mirror glass substrate from non-aqueous bath with ethylene glycol as a solvent, the temperature effect, structural morphology and optical properties of CdSe film deposited on mirror glass substrate have been studied.

EXPERIMENTAL

Cadmium Acetate [Cd CH$_3$COO$_2$] and selenium dioxide (SeO2) were used as sources of Cd and Se respectively. Tetra sodium salt of Ethylene Di Amine Tetra Acetic acid (EDTA) is used as complexing agent in bath solution. Mirror Glass substrate ultrasonically cleaned with double distilled water & dried in hot air oven . The polarization curves
were recorded at various bath temperatures on deposition potential was studied. PEC cell was fabricated using three electrode configuration, comprising n-CdSe thin film as a photo anode (Area, 1 cm²), Graphite as counter electrode & SCE as reference electrode & redox electrolyte is 0.1 M Poly sulphide solution (0.1 M NaOH + 0.1 M Na₂S + 0.1 M Sulphur). A 200 Watt Tungsten filament lamp was used as a light source. To prevent heating of the cell, Water filter was used in between the lamp & the PEC cell. To optimize the bath temperature, the ISC & Voc generated in the PEC cell under illumination of light were measured at various bath temperatures. To optimize deposition time, the films were deposited using optimized bath temperature for different time intervals. The deposited ultra thin film used for structural, Optical & Morphological Characterization, XRD patterns of the ultra thin films were obtained with the help of a Philips X-ray diffractometer (Model 1710) Cr Kα radiation. The surface morphology was studied by using scanning electron microscope using magnification of 5000 at potential 20 KV. The optical absorption studies were carried out with a UV-VIS-NIR spectrophotometer (model Hitachi in the wave length range 380-950nm).

RESULTS AND DISCUSSION

Deposition potential

Fig. 1 shows that cathodic polarization curve for mirror glass substrate in 5 ml 0.01m Cadmium Acetate [Cd CH₃COO₂] and 5 ml 0.005 m SeO₂ + 0.5ml 0.1M EDTA solution at 75°C temp.
Fig. 5: Shown that XRD pattern of ultra thin film of CdSe at 75°C temp

The graph shown that the deposition potential of CdSe lies between those of elemental Cd & Se (Yesugade et al 1995) & deposition potential (VISCE) values for mirror glass substrate is – 1.189 volt. & current density value is 0.38 mA/cm² and corresponding values of current efficiency are 74.35 %

Effect of temperature

Fig. 2 shows DC electro deposited catholic polarization curves for mirror glass substrate in the temperature, Range of 65 to 85°C in 5 ml [0.01M Cd (CH₃COO)₂ + 0.5 ml (0.1 M EDTA) & 0.005M SeO₂ (5ml) at difference bath temperature & corresponding deposition potentials are shown in the following Table:1, It is observed that deposition potential decreases with increase in the bath temperature.

Fig. 6: Plot of variation of (ghυ)² VS hi for CdSe ultra thin film deposited on mirror glass substrate on 75°C temp

Fig. 7: Shown that a surface morphology of the optimized temperature deposited film
Generally, increase in temperature increases the grain size & increasing grain size corresponds to a decrease in polarization potential at higher temperature (Brenner 1963). The increase in temperature dissociates the complex (Marcus 1952) & hence the concentration of simple metal ions increases, leading to the discharge of ions at a lower potential. Also, the rise in temperature of the bath enhances the rate of diffusion & increases the ionic mobilities & hence the conductivity of the bath increases (Jundale & Lokhande 1994).

### Table 1: Effect of bath temp. on deposition potential for bath composition used on glass mirror substrate.

| S. No | Bath Temperature (°C) | Deposition Potential (V / SCE) |
|-------|-----------------------|-------------------------------|
| 1     | 27                    | -1.72                         |
| 2     | 65                    | -1.25                         |
| 3     | 75                    | -1.18                         |

### Table 2: Comparison of observed & standard d values for CdSe films deposited on mirror glass substrate

| S. No. | Observed d (Å) | Standard d (Å) | Plane hkl |
|--------|----------------|----------------|-----------|
| 1      | 3.4897         | 3.5050         | 002       |
| 2      | 2.1389         | 2.1495         | 110       |
| 3      | 1.7896         | 1.7992         | 102       |

**PEC fabrication**

CdSe / 0.1M polysulphide / Graphite PEC cell constructed & check the conductivity of ultra thin film. By using 200 W Tungsten filament lamp with water compartment & it is seen that Isc & Voc increases initially with increase in bath temperature becomes maximum at a particular temperature 75°C & then decreases with further increase in temperature (Bhardwaj et al 1984). This variation in Isc & Voc at lower & higher values of bath temperature other than optimized one is attributed to he resistivity of CdSe thin films (Pawar et al 2006) optimized temperature’s ISC & Voc graph shown in Fig: (3)

**Thickness measurement**

Weight difference method is used for measurement of ultra CdSe thin film measurement. The variation of film thickness with deposition time is shown in fig :4 , It is observed that the deposition time increases, film thickness also increases, attains maximum thickness & thereafter decreases slightly with further increase in deposition time. This is attributed the maximum thickness is 0.688µm (Lade et al. 2000) (Optimized time = 35 min) for 75°C temperature.

**XRD analysis of CdSe Ultra Thin Film**

Structural properties of CdSe thin film were studied by using X-ray diffraction method. The structure of CdSe thin film is cubic zinc blend type structure or hexagonal structure & it is shown in Fig. 5, XRD patterns revealed that the films are polycrystalline in nature with hexagonal phase (JCPDS card Number 77-2307). Shows a comparison of observed d values of ultra thin film of CdSe with standard d values from JCPDS data files. Some peaks of substrates were also observed in the XRD pattern (JCPDS card Number 33-0397, 34-0396, 44-1294 & 77-0448). The plane 002 at 2θ (38° ) is Hexagonal phase is observed in XRD pattern. Table 2 Comparison of observed & standard d values for CdSe films deposited on mirror glass substrate.

**Optical analysis of CdSe Ultra Thin Film**

Optical Analysis of CdSe ultra thin film deposited on mirror glass substrate, The transmission data were used to calculate the absorption coefficient (α) using Tauc’s relation (Manifacier et al 1977):

\[ \alpha V = A ( h \alpha E g )^{1/2} \]
Where \( h\nu \) is the photon energy, \( E_g \) is the band gap & \( A \) is constant. Further absorption coefficient \( (\alpha) \) can be simplified as

\[
\alpha = -\ln \frac{T}{t}
\]

where \( T \) is the transmission & \( t \) is the thickness of the film which is 0.688 \( \mu m \).

The variation of \( (\alpha h\nu)^2 \) Vs \( h\nu \) for CdSe is linear at the absorption edge, Fig 6 which is shown that ultra thin film of CdSe having direct band gap semiconductor. Extrapolating the straight line portion of the plot of \( (\alpha h\nu)^2 \) Vs \( h\nu \) for zero absorption coefficient value gives the band gap which is found to be 1.70 eV.

**SEM Analysis**

The surface morphology of ultra thin film of CdSe was studied by SEM picture.

Fig:7 shown that a surface morphology of the optimized temperature deposited film & it is exhibiting its microstructure well adherent & grains are uniformly distributed over the surface of substrate.

**CONCLUSION**

The above studies shown that, it is possible to use mirror glass substrate for CdSe thin film deposition by using DC electro deposition technique. Film deposited from non-aqueous bath using ethylene glycol as a solvent. Decrease in deposition potential with increase in bath temperature was observed. PEC studies it is clear that CdSe is an n-type semiconductor material & it is suitable for solar cell. XRD study revealed the polycrystalline nature of the films with hexagonal phase. Optical absorption study showed that CdSe is a direct band gap material having a band gap energy of 1.70 eV. Surface Morphology shown that deposited film is well adherent & grains are uniformly distributed over the surface of substrate.

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**REFERENCES**

1. Brenner A. Electro deposition of Alloys, Academic press, New York, 677 (1963).
2. Brenner A., Electrode deposition of Alloys (New York) academic press 139 (1963).
3. Marcus H., Met. Finish 954 Muller MA & Gintey D.S. 1980 J.Mater. Sci. 151 (1952).
4. Jundale S.B. & Lokhande C.D. Mater Chem. Phys. 38: 325 (1994).
5. Bhardwaj R.C., Jadhav C.M. & Taqui Khan M.M., Solar cells : 293 (1984).
6. Pawar S.M., Moholkar A.V., Rajpure K.Y. & Bhosale C.H., J.Phys. & Chem. Solids 67: 2386 (2006).
7. Lade S.J., Upame M.D. & Lokhande C.D., Mater Chem. Phy 63: 99 (2000).
8. Manificer J.C., demurci a M fillard J.P. & Vicario E, Thin solid films 41: 127 (1977).
9. JCPDS Date files, 33-0397, 34-0396, 44-1294, 77-0448, 77-2307
10. Pandey R.K., Kumar S.R. & ROOZ AJN 1991, Thin solid films (2001).
11. Gutierrez M.T. & Ortega J., J. Electron Chem. Soc 138: 2316 (1989).
12. Baranski A.S. & Fawcett W.R., J. Electrochem. Soc 127: 166 (1980).
13. Baranski A.S. Fawcett W.R., Gatner K., Mc Donald A.C., Mc Donald J.R. & Selen M J (1983).
14. Skyllas – Kazacos M & Miller B, J. Electrochem. Soc 127: 2378 (1980).