Properties of pulsed electrodeposited CdSe thin film on fluorine tin–oxide (FTO) coated glass using aqueous bath

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ABSTRACT

Thin films of CdSe were deposited by electrodeposition technique on substrate of fluorine tin–oxide (FTO) coated glass using aqueous bath solution containing 0.02 M CdSO₄ (10 mL) + 0.2 M EDTA (1 mL) + 0.010 M SeO₂ (10 mL) at 75°C temperature. The preparative parameters were optimized to get good quality CdSe thin films. These films were characterized by X-ray diffraction (XRD), optical absorption and photoelectrochemical (PEC) techniques. The XRD analysis of the deposited film showed presence of polycrystalline in nature with hexagonal structure. The surface morphology studies by scanning electron microscope (SEM) shows that the deposited film are well adherent and grains are uniformly distributed over the surface of substrate.

Key word: Electrodeposition; XRD; CdSe thin films, SEM, Fluorine tin oxide.

INTRODUCTION

Recent investigation has shown that layered type semi conducting cadmium chalcogenide group which absorbed visible and near IR light are particularly promising materials for photoelectrochemical solar cell. Cadmium selenide having suitable band gap (1.74 eV) and high photosensitivity in the visible region of the spectrum can be utilized in a number of optoelectronic devices such as PEC cells (Muller and Ginley 1980), photoconductors (Nair et al., 1993), thin film transistors (Claster et al., 1998), gamma ray detectors (Roth 1989), etc.

Methods electrodeposition is an isothermal process mainly controlled by electrical parameters, which are easily adjusted to control film thickness, morphology, composition, etc. Literature survey shows that extensive work has been done on the preparation and characterization of CdSe thin films electrodeposited from aqueous acidic baths. The present study deals with preparation of CdSe thin films by electrodeposition method on FTO coated glass from aqueous bath. The influence of deposition parameters on the performance of PEC cell are of great scientific importance (Pawar et al., 2006). In view of this, a PEC cell of configuration n-CdSe/1M polysulphide/graphite is fabricated.

EXPERIMENTAL

CdSe thin films were electrodeposited on a substrate of fluorine tin–oxide (FTO) coated glass using aqueous bath containing 0.02 M CdSO₄ (10 mL) + 0.2 M EDTA (1 mL) + 0.010 M SeO₂ (10 mL) at 75°C temp. With saturated calomel (SCE) as reference electrode and graphite as counter electrode. Cadmium sulphate [CdSO₄] and selenium dioxide (SeO₂) were used as sources of Cd and Se, respectively. Tetra sodium salt of ethylene diamine tetra acetic acid (EDTA) was used as a
complexing agent. Prior to the deposition, the florine tin-oxide (FTO) substrates were washed with liquid detergent (Colin) followed by ultrasonic cleaning with double distilled water. In order to remove oily substance from the surface, cleaned substrates were etched in 0.5% \( \text{H}_2\text{SO}_4 \) for 5 min and finally ultrasonically cleaned with double distilled water. Then boiled in chromic acid for 30 min and ultrasonically cleaned with double distilled water and dried with hot air oven. The polarization curves were recorded 75°C temperatures to estimate the deposition potential. PEC cell was fabricated using 3-electrode configuration, comprising \( n\text{-CdSe} \) thin film as a photo anode \((A = 1\text{cm}^2)\), graphite as counter electrode and SCE as reference electrode. The redox electrolyte was 1M polysulphide \((\text{NaOH} + \text{Na}_2\text{S} + \text{S})\). A 200-Watt tungsten filament lamp was used as a light source. To prevent heating of the cell, water filter was interposed between the lamp and the cell. To optimize the bath temperature, the short circuit current (Isc) and the open circuit voltage (Voc) generated in the PEC cell under illumination of light were measured at 75°C bath temperatures. To optimize deposition time, the films were grown at the optimized deposition potential of 980 mV with respect to SCE and at the current density is 0.4 mA/cm². The deposited film have been dried and preserved in a desiccator for further study. The PEC cell, n-CdSe / Polysulphide / C is illuminated with a 200 W tungsten filament lamp. The photon having energy equal to or greater than the band gap energy of CdSe are absorbed in the semiconductor and the electron hole pairs are generated. These electron hole pairs are separated by local electric field present across the interface between semiconductor and polysulphide electrolyte. This leads to generation of the photo voltage under open circuit and photocurrent under short circuit condition.

Fig 2 shows the variation of Isc and Voc with deposition temperature from the graph, it is observed that Isc and Voc increases with increase in deposition temperature, attains maximum values for film deposited at 75°C temperature, on further increasing deposition temp. both Isc and Voc decreases. This indicates the formation of the good

### RESULTS AND DISCUSSION

#### Preparative Parameter

Optimization of preparative parameters for deposition of good quality and stoichiometric CdSe thin film is most essential. The polarization curve were plotted to determine the deposition potential of CdSe thin film form their respective volume ratio \((0.02 \text{ M CdSO}_4 (10 \text{ mL}) + 0.2 \text{ M EDTA (1 mL)} + 0.010 \text{ M SeO}_2 (10 \text{ mL}) at 75°C temp.)\) and it is shown in fig 1.

The films were grown at the optimized deposition potential of 980 mV with respect to SCE and at the current density is 0.4 mA/cm². The deposited film have been dried and preserved in a desiccator for further study. The PEC cell, n-CdSe / Polysulphide / C is illuminated with a 200 W tungsten filament lamp. The photon having energy equal to or greater than the band gap energy of CdSe are absorbed in the semiconductor and the electron hole pairs are generated. These electron hole pairs are separated by local electric field present across the interface between semiconductor and polysulphide electrolyte. This leads to generation of the photo voltage under open circuit and photocurrent under short circuit condition.

![Fig. 1: Variation of current density with applied voltage (polarization curve)](image1)

![Fig. 2: Shows the variation of Isc and Voc with deposition temp](image2)
Fig. 3: Shows the variation of Isc and Voc with Deposition time

Fig. 4: The thickness of the film

Fig. 5: X-ray diffraction patterns of CdSe film

Fig. 6: Plot of variation of $(\alpha \nu)^2$ VS $(\nu \nu) \nu$ for CdSe film

Fig. 7: SEM photograph of CdSe thin film
quality and almost stoichiometric compound at 75°C. Fig 3 shows the variation of Isc and Voc with Deposition time, which shows that Isc and Voc are maximum at 35 min. This indicates that the formation of good quality and almost stoichiometric compound at 35 min. The thickness of the film was measured by weight difference method assuming the density of the deposited film to be same as that of the bulk. The variation of film thickness with deposition time is shown in figure 4. It is observed that as deposition time increases, film thickness increases, attains maximum thickness and thereafter, decreases slightly with further increase in deposition time. This is attributed to the increase in the rate of dissolution than the rate of deposition after attaining the maximum thickness (Lade et al 2000). Structural properties of CdSe thin films were studied by X-ray diffraction. CdSe can form the hexagonal, wurtzite type structure or the cubic, zincblend-type structure. Fig 5 show XRD patterns of CdSe films deposited on FTO coated glass substrate. XRD patterns revealed that the films are polycrystalline in nature with hexagonal (JCPDS card number 77-2307) phase. Table 1 shows a comparison of observed ‘d’ values of CdSe films with standard ‘d’ values from JCPDS data files. Plane (002) at 2θ ~ 38° of hexagonal phase is observed in all the XRD patterns. Some peaks of substrates

Table 1: Comparison of observed and standered ‘d’ values for CdSe film

| S. No | Substrate             | Standered ‘d’ values (Å) | Observed ‘d’ value (Å) | Planes (hkl) |
|-------|-----------------------|--------------------------|-----------------------|--------------|
| 1     | FTO coated glass      | 3.5050                   | 3.4939                | 0 0 2        |
|       |                       | 2.1495                   | 2.1389                | 1 1 0        |

(JCPDS card number 33-0397, 34-0396, 44-1294 and 77-0448) were also observed in all the XRD patterns.

Crystallite size of CdSe film was calculated by using Scherrer’s formula,

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

where D is the crystallite size, \( \lambda \) the X-ray wavelength used, \( \beta \) the angular line width of half maximum intensity, \( \theta \) the Bragg’s diffraction angle and K some constant with a value of 0.9. The D values are also given in table 1. It shows that the crystallite size of CdSe films deposited on FTO coated glass substrate is large. Generally, ‘efficient’ electro crystallization means obtaining of compact, crystallized layers. However, high crystallinity may not always be the main objective, at least in view of a high PEC solar cell efficiency. The substrate state deposition plays an important role in this matter, since, together with potential, it determines the outcome of the process in terms of grain size and structure (Bouroushian et al 2000). In our case, deposition potential is more negative for CdSe thin film deposited on FTO coated glass. When deposition potential becomes more negative, larger current densities lead to growth of larger particle sizes (Shen et al 2005). The other possible reason might be the value of optimized bath temperature is 75°C for FTO coated glass substrate. The optical absorption of the film was studied in the wavelength range 340-860 nm, at room temp. for the film deposited on FTO coated glass substrate. The variation of optical absorption coefficient with wavelength was further analysed to find out the nature of the electronic transition across the optical band gap. The nature of the transition was determined by using the relation (Mathew, 2000, Mathew and Sebastian, 1999).

\[ \alpha = A \left( \frac{h \nu - E_g}{h \nu} \right)^n \]

Where

\( A = \) a constant
\( n = \frac{1}{2} \) for allowed direct transition.
Fig-6 shows the variation of \((\alpha h^\nu)^2\) with \(h_i\) for typical sample deposited at optimized preparative parameters (Deposition time 35 min and 75°C). It is linear, indicating the presence of direct transition. The straight portion is extrapolated to energy axis at \(\alpha =0\), which gives the band gap energy of CdSe to be 1.78 eV. The optical band gap of CdSe thin film in the present case is higher than the value for single crystals which is in accordance with the earlier observation on chemically deposited CdSe thin films (Nair et al 1993).

CONCLUSIONS

CdSe films can be electrodeposited on FTO coated glass in aqueous bath. From PEC studies it is clear observed, CdSe is an n-type material. X-ray diffraction study revealed the polycrystalline nature of the films with hexagonal phase. In addition, the crystallite size for hexagonal (002) plane is large. An optical absorption study showed that CdSe is a direct band gap material having band gap energy of 1.78 eV.

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