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Characterization of Electrodeposited Cadmium Selenide Thin Films

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Abstract

Cadmium selenide (CdSe) thin films have been deposited on glass/conducting glass substrates using low-cost electrodeposition method. X-ray diffraction (XRD) technique has been used to identify the phases present in the deposited films and observed that the deposited films are mainly consisting of CdSe phases. The photoelectrochemical (PEC) cell measurements indicate that the CdSe films are n-type in electrical conduction, and optical absorption measurements show that the bandgap for as-deposited film is estimated to be 2.1 eV. Upon heat treatment at 723 K for 30 min in air the band gap of CdSe film is decreased to 1.8 eV. The surface morphology of the deposited films has been characterized using scanning electron microscopy (SEM) and observed that very homogeneous and uniform CdSe film is grown onto FTO/glass substrate. The aim of this work is to use n-type CdSe window materials in CdTe based solar cell structures. The results will be presented in this paper in the light of observed data.

Keywords: Cadmium selenide, Electrodeposition, Thin film.

I. Introduction

Thin films of II-VI compound semiconductors have attracted much interest of many researchers because they find applications in the solid-state physics. II-VI compound semiconductors have the band gap between 1-3 eV in the visible region and these semiconducting materials are used worldwide in optoelectronic devices. Cadmium selenide (CdSe) is one of such popular semiconductor materials in this group and its physical properties have been constantly investigated during recent years for both fundamental and practical aims. Its interesting properties make the material suitable for many potential applications in a variety of solid state devices such as solar cells, high-efficiency thin film transistors, light-emitting diodes, electron-beam pumped lasers and electroluminescent devices, etc[1].

Till today, many different techniques such as sputtering, spray-pyrolysis, electrodeposition[2-5] are used to prepare CdSe thin film. Among the various methods electrodeposition technique provides a simple root of synthesizing thin films because of its simplicity, low-cost experimental setup from an economical point of view. In addition, this technique could be used for the production of large-area thin film deposition without any high vacuum system. In view of this, an effort has been made to study the optical, structural and electrical properties of CdSe thin films prepared by electrodeposition method.

Considerable amount of works have been done on this material but still new approach is coming up to find simple route and to synthesize quality films for better performance. In considering the importance of these materials in the field of optoelectronic devices, particularly solar cells, here we report the study of high purity CdSe films using a home made two-electrode system of electrodeposition method.

II. Experimental Details

Substrate preparation

Poor adhesion and non-uniform films are common problems when depositing films onto smooth surface, as the contaminated surface provides nucleation sites facilitating the growth which results non-uniform film growth. Therefore, during the deposition of thin film, substrate cleaning is very important. Before depositing CdSe films, fluorinated tin oxide (FTO)/glass substrates were boiled using soapy distilled water for around 20 minutes and then rinsed with distilled water. To eliminate grease and other oily substances, substrates were rinsed with acetone. It is then boiled in distilled water for about 20 minutes. The substrates were then cleaned well using ultrasonic cleaning bath prior to film deposition.

Film deposition and chemical reaction

The electrolytic cell used in this work consisted of a glass/conducting glass as working cathode, high purity graphite rod as an anode and an aqueous electrolyte containing required ions of Cd and Se. A typical electrolyte contains 0.08M $CdCl_2.H_2O$ and 0.005M H_2SeO_3 for Cd and Se source, respectively. At first cadmium chloride was mixed with selenous acid in 100 ml distilled water in a beaker and kept it stirring until the entire solid dissolved in distilled water. Ammonium solution was mixed with the solution to control the pH value of the solution and is kept 1.9. The substrates were then immersed vertically into the deposition bath against the wall of the beaker containing the reaction mixture. During the electrodeposition, the electrolyte was continuously stirred at a moderate speed with the help of a magnetic stirrer. The deposition potential was fixed at a constant voltage 1.2 volt for about 40 minutes. After deposition, the glass substrates were taken out from the bath, washed with hot distilled water and were dried in blowing air and preserved for basic characterizations. In order to investigate heating effect, the as-deposited films were annealed at 723 K for 30 minutes in air.

Cadmium selenide films have been formed according to the following over-all reaction[6].

$$3Cd + H_2SeO_3 + 4H^+ \longrightarrow CdSe + 2Cd^{2+} + 3H_2O$$

In this mechanism, the first step is the reduction of H_2SeO_3 to selenium on the surface of the substrate according to the reaction

$$H_2SeO_3 + 4e^- + 4H^+ \longrightarrow Se^0 + 3H_2O$$

Which is at once followed by a successive reduction process

$$H_2SeO_3 + 4H^+ + 6e^- \longrightarrow H_2Se + 3H_2O$$

And lastly, formation of cadmium selenide takes place according to the chemical reaction

$$H_2Se + Cd^{2+} \longrightarrow CdSe + 2H^+$$

Film characterization

Photoelectrochemical (PEC) cell was used to determine electrical conductivity type of CdSe films where a CdSe/NaCl electrolyte (solid/liquid) junction was illuminated by white light. Optical absorption spectra for as-deposited thin films were obtained in the visible region (400 – 900 nm) using UV-VIS spectrophotometer (Model: UV-1201V, Shimadzu Corp., Japan). Surface morphology of the films were examined using JEOL JSM-6490LA model Scanning Electron Microscope (SEM) attached with an Energy Dispersive X-ray (EDX) system to measure the sample stoichiometry quantitatively. A Philips PW3040 X'Pert PRO X-ray diffractometer was used to characterize the films and to determine the structural parameters. The monochromatic (using Ni filter) CuKα radiation was used with primary beam power of 40 kV and 30 mA. All the samples were irradiated over 2θ range from 20° to 60° to get possible fundamental peaks of the sample with the sampling pitch of 0.02° and time for each step data collection was 1.0 sec. All the data of the samples were analyzed using computer software "X'PERT HIGHSCORE" from which structural parameters were determined.

III. Results and Discussion

Electrical conductivity type of CdSe films

PEC measurement was performed to identify the electrical conductivity type of CdSe films. A PEC cell was fabricated by two electrodes partially immersing in 10% NaCl solution. One electrode was CdSe-deposited FTO which forms a solid/liquid Schottky junction at CdSe/NaCl solution and the other was a purely carbon rod, and these electrodes were externally connected to a digital voltmeter. The open circuit voltage was measured under dark and illuminated condition produced by the CdSe/NaCl Schottky junction. The polarity of the voltage indicates the determination of conductivity type of CdSe film. It was observed that the as-deposited and annealed CdSe films are n-type in electrical conduction and conversion efficiency improves after annealing.

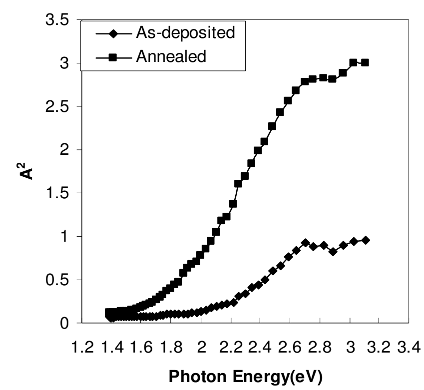

Fig. 1. Estimation of band gap (E_g) of as-deposited and annealed CdSe thin film.

Optical properties

CdSe thin film deposited on FTO-coated glass was characterized by optical absorption technique. The absorption data is further analyzed for near edge optical absorption of semiconductors using a classical relation, $\alpha = A^*(h\nu - E_g)^n / h\nu$, where the symbols have their usual meaning. A is a constant, $n = 0.5$ for direct transition. Figure 1 shows the variation of A^2 versus hν for CdSe thin films. The curve is linear at the absorption edge. Extrapolating the straight line portion of the A^2 versus hν plot to zero absorption coefficient gives the band gap energy (E_g) to 2.1 eV. The estimated value of band gap is greater than the standard band gap (1.7 eV) of CdSe material, showing a `blue shift' of 0.4 eV. Similar `blue shift' in E_g values for chemically deposited CdSe thin films with smaller thickness and/or grain sizes has been reported[7]. After annealing the sample at 723 K for 30 min in air caused a decrease in band gap to 1.8 eV. The decrease in band gap could be attributed to the increase in the grain size of the CdSe film. The effect of grain size on the optical band gap arises out of quantum confinement effects[8].

Surface morphology

Figure 2 shows SEM image of as-deposited cadmium selenide (CdSe) thin films on FTO-coated glass substrates; it consists of closely packed grains. It shows that the substrate is well covered with the deposited material without cracks and pinholes. The scanning electron microscopy (SEM) study for CdSe films on the FTO-coated glass substrates reveals that the films formed are homogeneous and uniform. The grain size of the CdSe thin films was observed to be 300-750 nm.

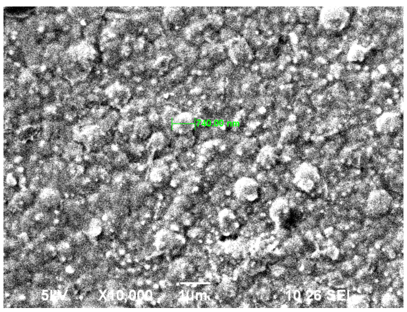

Fig. 2. SEM image of as-deposited CdSe thin film. Magnification 20000X.

Compositional analysis

The elemental analysis of CdSe thin films deposited on FTO-coated glass substrate was performed using EDX analysis and are presented in Fig. 3. It is noted that there are some oxygen, carbon and other contamination of the films that can be attributed to contamination of the surface, grain boundaries etc. of the film from the atmosphere[9].

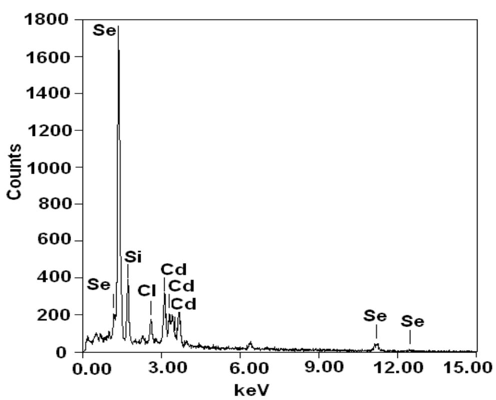

Fig. 3. EDX pattern of CdSe films on FTO surface.

Structural properties

X-ray diffraction studies were carried out on both substrate and the CdSe films in order to identify the bulk structure and the different phases present. Figure 4 shows the XRD spectra obtained for (a) glassy FTO substrate and (b) as-deposited CdSe films. Several well defined peaks are observed in the XRD pattern.The prominent peaks observed at (002) and (103) planes. Comparison of the spectra with reference code 00-002-0330 of JCPDS data identifies two strong peaks arising from the CdSe film[10]. These (002) and (103) reflections correspond to the hexagonal CdSe phase. The matching of observed "d" values with standard ones is given in Table-1, which confirms the formation of CdSe material.

Table. 1. Comparison of standard and observed "d" values for electrodeposited CdSe thin films on FTO.

Observed d-spacing (Å)	Standard d-spacing (Å)	(hkl) planes
3.50867	3.52	002
2.03144	1.99	103

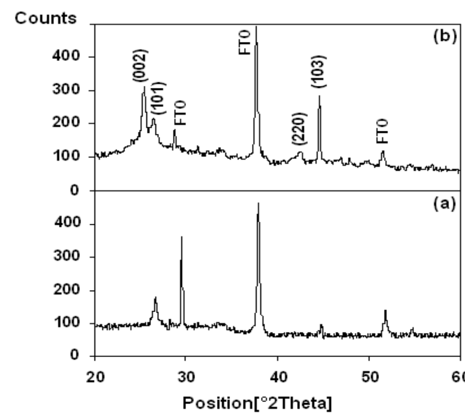

Fig. 4. X-ray diffraction pattern of (a) FTO surface and (b) as-deposited CdSe film.

IV. Conclusions

Good quality thin films of smooth surface of cadmium selenide are electrodeposited using cadmium chloride as a source of cadmium ions and selenous acid as a source of selenium ions in an acidic aqueous bath. It is clear from PEC measurement that the CdSe films are of n-type in electrical conductivity. The absorbance of the CdSe films increases continually from the near-infrared towards the visible region, which makes this material suitable for use in infrared (IR) detectors. The band gap of the CdSe thin films is found to 2.1 eV and 1.8 eV for as-deposited and annealed film, respectively. It is observed from SEM measurement that the substrates are well covered with the deposited CdSe material without cracks and pinholes. The grain size of the

CdSe films is observed to be 300-750 nm. The XRD analysis shows that the preferential planes of CdSe film are (002) and (103).

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