Deposition and characterization of cadmium indium selenide thin films by chemical bath technique

K. GIRIJA^{*}, S. THIRUMALAIRAJAN, S. M. MOHAN

Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore - 641 020, TamilNadu, India

Semiconducting n-type cadmium indium selenide (CdInSe) thin films have been deposited on glass substrate using chemical bath technique at temperatures 313 k, 333 K and 353 K respectively, due to their tailored properties than the individual elements find potential applications in optoelectronic devices. Studies on the structural properties of the films were carried out by X-ray diffraction and scanning electron microscopy techniques revealed the cubic structure and the surface morphology. The presence of elemental constituents was confirmed using energy dispersive X-ray analysis. From the transmittance spectra it was found that the transition was direct with band gap energy ranging between 2.28 eV-1.55 eV.

(Received December 20, 2008; accepted January 21, 2009)

Keywords: Thin films, Chemical synthesis, X-ray diffraction, Optical properties

1. Introduction

Cadmium indium selenide (CdInSe) is a semi conducting ternary chalcogenide possessing numerous technological applications in the field of solar energy conversion [1]. Others areas of successful application includes light emitting diodes, photo detectors, electrophotography, lasers, gas sensors, thin film transistors and gamma ray detectors [2]. CdInSe can be used in photo electrochemical devices because of their specific physical properties especially due to their direct band gap ranging from 2.28 eV-1.55 eV. Several physical and chemical techniques are available for the growth of CdInSe thin films. CdInSe thin films have been deposited using different techniques such as electro chemical deposition [3], spray pyrolysis [4], vacuum evaporation [5] and slurry pasting technique [6]. Among these methods CBD has several overriding advantages with other techniques such as uniform film deposition, control of thickness, precise maintenance of deposition temperature, low cost and can produce reproducible large-area thin films [7, 8]. In the present investigation CBD of CdInSe thin film on glass substrate has been reported. Structural characterization from XRD, EDAX, SEM and optical characterization from UV-Vis were carried out and discussed.

2. Experimental details

2.1 Film preparation

The reaction mixture was prepared by adding ammonia (NH₃) solution in 0.09 M of cadmium acetate $[(CH_3COO)_2Cd. 2H_2O]$ till a pH of 11 is attained. To the precursor solution 0.01 M of indium tri chloride (InCl₃) was added and then 5 ml of freshly prepared sodiumselenosulphite (Na₂SeSO₃) diluted with 5 ml of distilled water was added drop by drop under continuous gentle stirring with the help of magnetic stirrer at about 80 \pm 1 rpm. Na₂SeSO₃ was prepared by refluxing 4 gms of selenium powder with 12 gms of anhydrous sodium sulphite (Na₂SO₃) in 50 ml of double distilled demineralised water for 4 hours at 80 \pm 0.5 °C. Thoroughly cleaned glass substrates were vertically immersed at the centre of the reaction bath. The films were deposited at bath temperatures 313 K, 333 K and 353 K which was controlled using digital thermostat connected with Pt-100 thermocouple. The time of deposition was optimized as 130 minutes. After deposition the substrates were rinsed in double distilled water and dried. The films were then annealed in air at a temperature of 553 K for 15 minutes. Films prepared by this method were dark brown, uniform, well adherent to the substrate, smooth and reflecting.

2.2 Film kinetics

Deposition of CdInSe thin film occurs when the ionic product (IP) exceeds the solubility product (SP). The hydrolysis of Na_2SeSO_3 proceeds via the chemical reactions

$$Na_2SeSO_3 + OH^ \checkmark$$
 $Na_2SO_4 + HSe^-$
 $HSe^- + OH^ \checkmark$ $Se^{2-} + H_2O$

When ammonia is added to Cd^{2+} salt solution, $Cd(OH)_2$ is produced and precipitates when $Cd(OH)_2$ is exceeded but dissolves in excess of ammonia solution to form complex cadmium tetra-amine ions.

$$(CH_3COO)_2$$
 Cd. $2H_2O + 4$ NH₃ $(Cd (NH_3)_4)^{2^+} + (CH_3COO)_2^{2^-} + 2H_2O$

On addition of indium tri chloride, CdInSe thin film formation takes place.

$$\left[\operatorname{Cd}\left(\operatorname{NH}_{3}\right)_{4}\right]^{2+} + \operatorname{InCl}_{3} + + \operatorname{Se}^{2-} \longrightarrow \operatorname{CdInSe} + (\operatorname{NH}_{3})_{4}\operatorname{Cl}_{3}$$

2.3 Characterization

Structural characterization of CdInSe thin films by Xray powder diffraction was obtained using a JEOL JDX services instrument with CuK_a radiation (λ =1.5406 Å). The microstructures and elemental analysis of these samples were characterized using Hitachi S-3400 equipped with an EDAX spectrometer. The optical properties were measured using UV-Vis spectrophotometer (JASCO V-530 dual beam).

3. Results and discussion

3.1 Crystalline structure

The structural characterization of CdInSe film for bath temperatures 313 K, 333 K and 353 K are presented in Fig. 1 (a), (b), (c). In the XRD pattern, the presence of the prominent peaks correspond to reflections from (111), (220) and (311) planes [ASTM Data File No. 08-267] and the mathching of observed and standard d values [9] confirm the formation of CdInSe compound with cubic crystal structure.



Fig. 1 (a). XRD pattern of CdInSe (313 K) thin film;(b). XRD pattern of CdInSe (333 K) thin film; (c) .XRD pattern of CdInSe (353 K) thin film.

3.2 Surface morphology

The surface morphology of CdInSe thin film prepared at 333K is shown in Fig. 2 (a), (b). Nonuniform spherical shaped grains were observed from the micrograph. The average cluster size of the CdInSe particle was found to be 485 nm. Cracks observed on the surface region indicate that the films were less compact on glass substrate and it can be eliminated by increasing the mass thickness of the film.





(b)

Fig. 2. (a) and (b). surface morphology of CdInSe thin film.

3.3 Energy dispersive X-ray analysis (EDAX)

The EDAX pattern for bath temperature 333 K is shown in Fig. 3 which confirms the presence of cadmium, indium and selenide compounds. The average atomic percentage ratio of CdInSe was found to be 13.42: 0.22: 1.99 indicating that the sample was cadmium rich and indium deficient. The pattern exhibits peak belonging to silicon (Si), calcium (Ca) and oxygen (O) these are due to glass substrate used during deposition.



Fig. 3. EDAX pattern of CdInSe (333 K) thin film.

3.4 Optical properties

The optical transmittance spectra of CdInSe thin film as a function of wavelength in the range 400-1200 nm is shown in Fig. 4 (a). The material showed decrease in transmittance as the temperature increases along with the crystallinity nature. A typical plot of $(\alpha hv)^2$ with photon energy hv for bath temperatures 313 K, 333 K and 353 K are shown in Fig. 4 (b).



Fig. 4 (a). Transmittance spectra of CdInSe thin film; (b). Band gap energy of CdInSe thin film.

Extrapolation of straight line portion of the curve to zero absorption coefficient gives the band gap energy and was found to be 2.28 eV, 1.79 eV and 1.55 eV respectively. The reason for variation with other reported bandgap values are attributed to the crystal nature and deposition conditions of the films.

4. Conclusions

CdInSe thin films were deposited on glass substrate by chemical deposition technique at bath temperatures 313 K, 333 K and 353 K. XRD analysis confirmed that the films are polycrystalline in nature with cubic structure. SEM analysis revealed the presence of non-uniform spherical shaped clusters of average size 485 nm. The presence of elemental constituents was confirmed from EDAX analysis. The optical transition involved in the material is direct with band gap energy lying in the range 2.28 -1.55 eV.

Acknowledgements

The authors would like to acknowledge the Bharathiar University, coimbatore-641 046 and Pondicherry University for providing analytical facilities.

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*Corresponding author: kgirija1@gmail