Fabrication and Characteristics of Nano Sized ZnSe Thin Films by Chemical Bath Deposition

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ABSTRACT

Zinc selenide is a potential candidate for use as an n-type window layer in thin film heterojunction solar cells due to its wide band gap of 2.7 eV. ZnSe thin films were therefore, chemically deposited onto glass microslides at 70°C. The deposition time and reaction pH were monitored as 180 min and 10±0.5 respectively. Film thickness of ZnSe thin films was measured by an interferometer technique and is found to be 544 nm. The films were then characterized by the XRD, optical and Raman techniques. Structural studies on ZnSe showed that the films exhibit hexagonal wurtzite structure with <100> preferred orientation. The d-value and intensity of reflection have excellent match with that of the JCPD data. The lattice parameter 'a' is found to be 3.990 A° and 'c' is 6.560 A°. The average crystallite size using Debye Shirrer's method is 52 nm. The surface features revealed by SEM showed uniformly distributed crystallites and their spherical shape. Broad absorption edge of thin films was revealed with high absorption coefficient ($\alpha = 10^4$ – 10⁵ cm⁻¹). The optical bandgap (Eg) of ZnSe thin films is 2.682 eV. Raman spectra showed presence of LO mode at 248 cm⁻¹ and TO mode at 204 cm⁻¹.

Keywords: ZnSe, Chemical bath, Wurtzite, LO and TO modes.

INTRODUCTION

The II -VI polycrystalline semiconducting materials are under increased scrutiny because of their wider use in device cost reduction in the era of photovoltaics and high speed optoelectronics [1-2]. Due to nontoxicity, higher abundance, thermal and mechanical stability, zinc selenide is one of the most promising materials for the fabrication of the next generation of optoelectronic devices in the UV-Vis region [1-4]. Various deposition techniques have been widely used to produce zinc selenide thin films. However, seeking the most reliable and economic deposition technique is the main goal. The most intensively studied techniques include, chemical bath [1,5,6], RF magnetron sputtering, thermal evaporation [2], solgel method, pulsed laser deposition (PLD) and spray pyrolysis. Among these methods, chemical bath is the most useful technique for large area applications. This method is cheaper, simple and allows us to obtain films with high transparency and conductivity for optoelectronic applications [5]. Preparation of nontoxic, cost-effective and stable material is the need of society and its use in optoelectronic devices alternative to Cd free (eco-friendly) is necessity of nature [2,6].

METHODOLOGY

Preparation of the samples

ZnSe thin films were deposited by a chemical bath deposition on to glass substrate using AR grade zinc sulphate and sodiumselenosulphate as precursor. Glass substrates were ultrasonically cleaned by deionized water, acetone and methanol before the experiment. The volume of chemical bath contains zinc sulphate + ammonia + sodiumselenosulphate + water (10 + 10 + 20+60) ml solutions. The films were prepared at the deposition temperature 70° C, deposition time 180 min, pH 11 with equimolar (0.1 M) zinc sulphate and sodiumselenosulphate solutions.

Characterization of the samples

The film composition and surface morphologies were investigated by the EDS and SEM. A JEOL6360, JED2300 scanning electron microscope were used for these studies. The structural properties were studied by Philips X- ray diffractometer PW – 1710 (λ = 1.5405 A⁰) using Cu – K_x radiation in the range 20⁰ to 80⁰. Optical transmission at room temperature was recorded in the 200-900 nm wavelength range using a UV-Vis-NIR spectrophotometer. Raman spectra were obtained using Reinshaw microscope (514 nm He-Ne laser) in the spectral range from 150 to 320 cm⁻¹.

RESULT AND DISCUSSION

The ZnSe films obtained under the above conditions are homogeneous, tightly adherent with light brown colored tinge. Film thickness of ZnSe thin films is ~544 nm.

The EDS Studies

An energy dispersive X-ray spectroscopy (EDS) was employed to determine the quantitative measure of ZnSe thin film samples. The atomic % of Zn²⁺, Se²⁻ are 40.96 and 59.06 respectively. EDS analysis conferred presence of expected elements Zn and Se in the thin solid films. Fig 1 shows EDS spectra for ZnSe thin films.

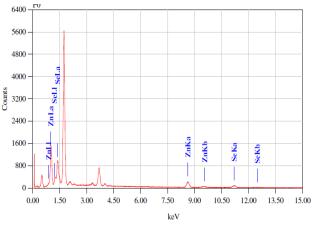


Figure 1. EDS Spectra of ZnSe Thin Films

Surface Microscopy

The surface morphology of the thin film layer was viewed through a scanning electron microscope at 20 KV is shown in Fig. 2. SEM micrograph showed that the crystallites are uniformly distributed and spherical in shape. A considerable fusing of crystallites has also been observed.

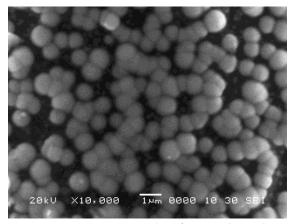


Figure 2 SEM Micrographs of ZnSe Thin Films

X-ray Diffraction

Structural characterization of the as-deposited samples was done using XRD analysis. Fig. 3 shows Xray diffractogram of ZnSe sample. Structural studies showed that the polycrystalline nature of the material and films exhibit hexagonal wurtzite structure with <100> preferred orientation. The average crystallite size calculated using Debye-Shirrer Equation is 52 nm. The lattice parameter 'a' is found to be 3.990 A° and 'c' is 6.560 A°.

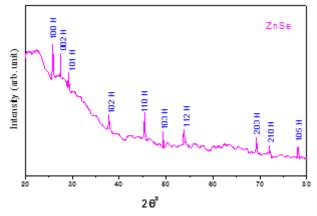


Figure 3. X-ray diffractograph of ZnSe Thin Film

Raman Studies

Fig. 4 shows Raman Spectra of ZnSe thin films. Raman spectra showed presence of LO mode at 248 cm⁻¹ and TO mode at 204 cm⁻¹. Existence of LO and TO modes confirmed formation of the ZnSe thin films. The presence of LO mode signify crystalline nature of the as-deposited ZnSe thin films.

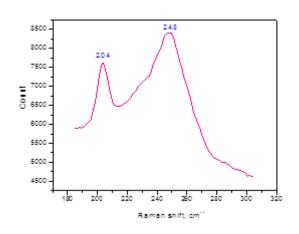


Figure 4. Raman Spectra of ZnSe Thin Films

Optical Studies

The optical band gap (Eg) was therefore determined for the film using (ahv) = A (hv-Eg) m, where m and A are constants, a is the absorption coefficient (cm⁻¹) and hv is the photon energy (eV). The Variation of $(ahv)^2$ vs hv of ZnSe thin film is shown in of Fig. 5. The optical band gap (Eg) of ZnSe thin films is 2.682 eV.

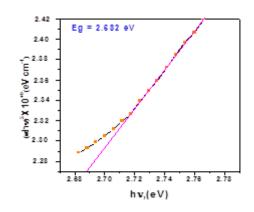


Figure 5. Variation of (ahv)² vs hv for ZnSe thin films.

CONCLUSION

ZnSe thin films were successfully deposited on glass substrates by a liquid phase chemical bath deposition. The formation of ZnSe thin film layers was confirmed by the EDS. ZnSe solid thin films are polycrystalline in nature and exhibit hexagonal phase with growth orientation <100>. Existence of LO and TO modes confirmed formation of the ZnSe thin films. The optical band gap of thin films is 2.682 eV and useful for photovoltaic studies.

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