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Structural, morphological and optical studies of ZnSe thin films: Growth using chemical bath

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ABSTRACT

Wide bandgap ZnSe (Eg=2.7 eV) films were grown under increasing influence of reducing atmosphere with 70 ^{0}C growth temperature, 210 min deposition time and pH equal to 10±0.2. The concentration of hydrazine hydrate in the bath was therefore varied and film stoichiometry (Zn/Se ratio) was determined from the EDS observations on the films (0.993 to 0.570). All the films exhibited wurtzite structure with preferred <101> orientation. AFM (3D) images showed that the surface roughness varied from 0.451 μm to 0.155 μm as Zn/Se ratio decreased. The reflectance spectra gave decrease in the band gap (2.69 eV to 2.55 eV) with decrease in Zn/Se ratio.

Keywords: ZnSe, CBD, Hi-Tech material, hexagonal wurtzite, spherical crystals.

INTRODUCTION

In recent years, II-VI DMS thin film materials have attracted tremendous attention in their fundamental studies as well as in technical worldwide applications due to their unique size dependent properties that are distinct from their corresponding bulk characteristics. In addition, a drastic cut in the production cost of these DMS semiconductor thin films in place of single crystals has been observed [1-5]. Materials Science encompasses various classes of materials; among them chalcogenides containing S, Se or Te are a recognized group of inorganic materials which constitute a rich family of semiconductors [6]. Direct wide band gap ZnSe (2.7 eV) would be a perfect match for short wavelength optoelectronic device applications especially, for blue laser diodes, light emitting diodes, laser screens, thin film transistors, photo detectors, photovoltaic cells and ZnSe based hetero structures for solar cells [1-10]. Wide band gap coupled with an optical transparency (>80%) over a wide range make it suitable for window layer and buffer layer in CIGS solar cells and absorbers [1-11]. The ZnSe films were therefore prepared and investigated by the various growth techniques, such as chemical bath deposition (CBD) [4, 5, 7, 12-15], electron beam evaporation [8, 9], thermal evaporation [10], chemical vapour deposition (CVD) [16], atomic layer deposition [17], electrodeposition [18], sol-gel method [19], etc and their different properties have been studied. These films as a buffer layer have better conformity of lattice parameters to that of CIGS, non-toxicity and possibilities of obtaining large area production at lower cost and processing temperature [4, 5, 12-15]. A very attractive method in this respect is the chemical bath deposition [4, 5, 12-15]. Structural, morphological and optical properties of these films have been studied through the XRD, AFM and UV-Vis techniques and are reported in this paper.

MATERIALS AND METHODS

Preparation of the samples

The ZnSe thin film layers were obtained onto the spectroscopic grade glasses from a liquid phase consisting of AR quality 0.5M $ZnSO_4$ and 0.25M sodium selnosulphate as the precursors and at the deposition temperature of 70°C, time equal to 210 min and pH around 10±0.25 [12], Complexing agent, 25% aqueous NH_3 and 80% $(NH_2)_2$ H_2O as reducing agent (varied from 3-12 ml) were used to obtain good quality thin films [12]. The as-deposited films were characterized through the composition, structure, surface morphology and optical characteristics.

Characterization of the samples

The film composition and surface morphologies were then investigated by the EDS and AFM techniques. The JEOL6360, JED2300 scanning electron microscope and diCaliber-Veeco atomic force microscope (in both trace and reference information) were used for these studies. The crystalline nature and structure were determined by an X-ray diffraction technique (Bruker-AXS-D8, Cu/40kV/40mA) with CuKα line (λ= 1.5406 Å). The range of 2θ values was from 20° to 80°. Optical transmission at room temperature was recorded in the 200 nm-2500 nm wavelength range using a UV-Vis-NIR spectrophotometer.

RESULTS AND DISCUSSION

Compositional analysis

For chemical deposition of ZnSe, growth kinetics suggests that, ammonia provides an alkaline environment whereas release of Se^{2-} ions is solely controlled by the hydrazine hydrate and therefore film composition is decided by the concentration of hydrazine hydrate in the bath [4, 12]. In this experiment, ZnSe films were obtained for a varying concentration (3ml-12ml) of hydrazine hydrate in the bath [12] and for each of the samples, an average composition was determined by an EDS technique shown in Table.1.

Table I: An EDS analysis of ZnSe films deposited for various concentration of hydrazine hydrate (P- ml Sample).

Sample		P3	P4	P5	P6	P7	P9	P10
Mass %	Zn	49.82	49.65	48.88	45.86	44.40	43.63	36.47
	Se	50.18	50.35	51.12	53.14	55.60	56.37	63.53
Zn/Se ratio		0.993	0.98	0.94	0.86	0.79	0.77	0.57

Analysis of the spectra showed that the Zn-content in the film typically decreased from 49.82 at% to 36.47 at% whereas Se-content increased from 50.18 at% to 63.53 at% as Zn/Se ratio was varied from 0.993 to 0.57. Crystal growth is nearly stoichiometric for low concentration of hydrazine hydrate whereas, enhanced rate of reduction at higher concentration of hydrazine hydrate led to the non stoichiometric deposits.

Structural properties

The structure of these films was then determined using an XRD analysis. All the samples are crystalline hexagonal wurtzite type phase with growth orientation along <101> [12]. The d-values and I/Imax values nearly match with that of the JCPD data [20]. A little decrease in lattice parameters (a and c) has been observed as shown in Fig. 1(a). Fig. 1(b) also shows variation of interplanar distance (d) with Zn/Se ratio. d is found to be considerably decreased with Zn/Se ratio. The crystallite sizes were then determined for all the samples and found to be decreased continuously from 67 nm to 55 nm as the Zn/Se ratio was decreased from 0.993 to 0.570.

AFM Analysis

Surface topological features of different Zn/Se ratio samples as-observed under AFM (3D) are shown in fig. 2. The films exhibit an uniform surface with spherical dip embedded, fine grains. The surface roughness, RMS average value and heights were determined. The surface roughness varied from 0.451 μm to 0.155 μm. Initially, when Zn/Se ratio is high, crystallites appear to be nearly spherical with slightly bigger in size and growth proceeds with formation of hillocks and valleys. Surface roughness is more in this case (micrograph a). As the Zn/Se ratio is decreased, hillocks collapse and surface becomes smooth. This is clearly seen from the micrographs c and d. RMS average values and average heights varied from 0.092 μm to 0.007 μm and 0.309 μm to 0.226 μm, respectively. Average height is an indicative of size of the hillocks and valleys.

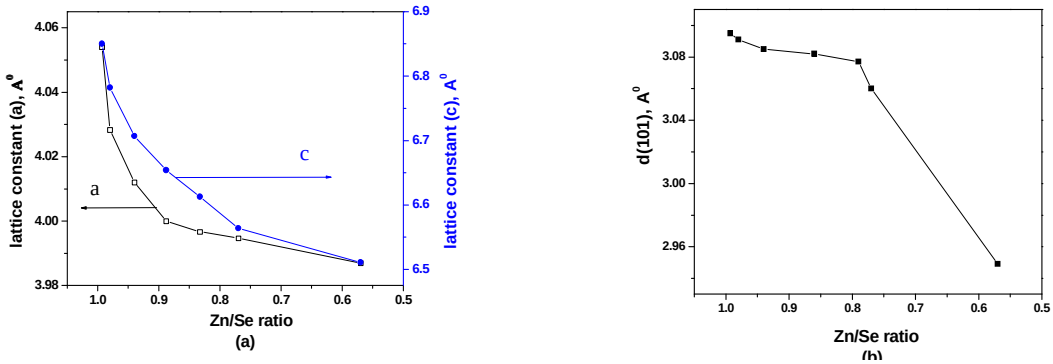

Fig. 1. Variation of (a) lattice parameters and (b) d values with Zn/Se ratios
a) Zn/Se = 0.993, b) Zn/Se = 0.94, c) Zn/Se = 0.79,d) Zn/Se = 0.77 and e) Zn/Se = 0.57

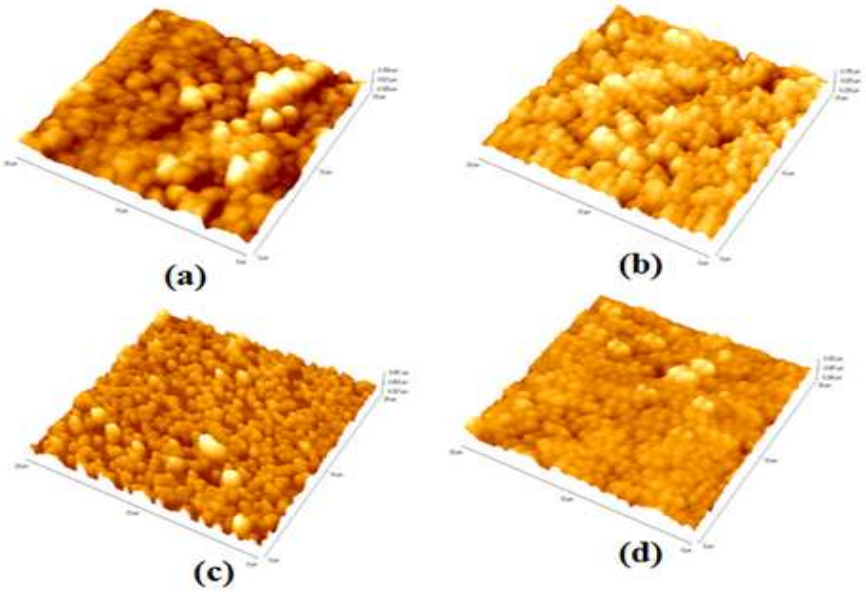

Fig. 2. 3-D AFM images of as-deposited ZnSe thin films.
a) Zn/Se = 0.993, b) Zn/Se = 0.79, c) Zn/Se = 0.77 and d) Zn/Se = 0.57.

Optical studies

The variation in optical transmittance was recorded in the wavelength range from 200 nm to 2500 nm for all the films. Fig.3 shows variation in %T with wavelength (λ). The transmittance spectra showed minimum transmission at shorter wavelengths whereas maximum transmission in the higher wavelength range and the transmission edge is not sharp as expected for thin films. The edge is found to be shifted towards longer wavelength side as Zn/Se ratio is decreased. The optical gaps were then calculated for all the film compositions and its variation with Zn/Se ratio is shown as inset in Fig. 3. The band gap of ZnSe is found to be decreased from 2.69eV to 2.52 eV as the ratio Zn/Se was decreased from 0.993 to 0.570. It appears that, for nearly stoichiometric ZnSe, the band gap is higher and it decreased down as the film stoichiometry is decreased. The variation of band gap with Zn/Se ratio seems to be contradictory with the literature, because in our case particle size is found to be decreased with decrease in Zn/Se ratio. Obviously band gap should increase due to size quantization. In our case, the variation in band gap can be correlated to the compositional studies of these films, wherein Zn^{2+} is replaced from the lattice by the hydrazine hydrate. In effect, films are selenium rich and presence of excess metallic selenium phase in the film may be the probable reason to decrease the band gap. This can further be supported by the observed conductivity measurements on these films wherein the electrical conductivity is found to be increased considerably with decrease in Zn/Se ratio.

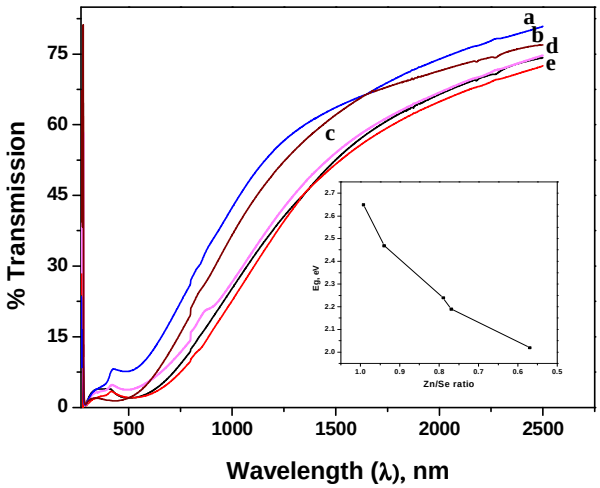

Fig.3. %T vs λ for ZnSe films of various ratios: Inset (Variation of Eg vs Zn/Se ratio)
a) Zn/Se = 0.993, b) Zn/Se = 0.94, c) Zn/se = 0.79, d) Zn/Se = 0.77 and e) Zn/Se = 0. 57.

CONCLUSION

In conclusion, excellent quality ZnSe thin films can be grown under the influence of hydrazine hydrate. The films exhibit wurtzite hexagonal phase with growth orientation along <101>. The films exhibit an uniform surface with spherical dip embedded, fine grains. The reflectance spectra gave a decrease in the band gap (2.69 eV to 2.55 eV) with decrease in Zn/Se ratio. A resulting bandgap of 2.55eV is a technically fit for PV- applications as an absorber material.

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