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Influence of annealing on the characteristics of nanostructure ZnSe thin films

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Abstract: ZnSe thin films of thickness of 200 nm are deposited by vapor deposition technique and later annealed in argon at 100°C and 300°C. XRD reveals that the grain size of ZnSe phase increases with the annealing temperature. The Raman spectrum shows peaks corresponding to LO mode of ZnSe and the intensity of Raman peaks is found to increase with increasing grain size. The optical studies correspond to band gap for ZnSe and the value of band gap is found to decrease with increasing annealing temperature which could be attributed to the quantum confinement effect.

Introduction

ZnSeis anII–VI wide band gap semiconductor that has the advantages of being highly resistive and UV lightsensitive¹ which is extensively used in Ultra-violet (UV) imaging technology. ZnSe thin films are extensively used in fabrication of various optoelectronic devices such as photo electrochemical cells, solar cells, thin film transistors, light emitting diodes (LED's), blue laser diodes, photo diode, dielectric mirrors etc^{1,2,3}. There are various techniques often used for deposition of ZnSe thin films such as chemical bath deposition (CBD) technique⁴, sputtering⁵, and vacuum evaporation technique⁶. Thermal evaporation is the simplest and widely used technique for preparation of thin solid films for technological applications. In the present investigation, ZnSethin films of 200 nm thickness are deposited on a fused silica substrate and are annealed in argon atmosphere at 200°C and 300°C. Effects of the post deposition annealing on the film properties such as grain size; phase formation and optical properties are discussed.

Experimental

ZnSe films are deposited on fused silica substrates by vacuum evaporation technique by evaporating 99.99% ZnSe powder. The substrate dimensions are 1cm x 1cm x 1mm and the filmthickness is 200 nm. These films are annealed at 400°C in argon atmosphere at two different temperatures 200°C and 300°C. Argon is chosen as the ambient as to avoid contamination from the air atmosphere resulting in formation of native oxide layer. The post deposition annealed films are characterized by X-ray diffraction and Raman spectroscopy for phase formation studies and UV-Vis spectroscopy for band gap calculation. The XRD is performed using Cu-K α radiation with λ = 1.5418 A on a PhillipsPanalyticalXpert Pro MPD spectrometer. The samples were scanned for the 2 θ of 20°-80° and were rotated at a speed of 0.0006°/Sec. UV Vis spectroscopy measurements

are done by with a UV-VIS double beam spectrophotometer CARY 5000and Raman spectra is obtained by Reins haw In via Raman microscope.

Results and Discussions

XRD Studies

X-ray diffraction (XRD) is used to determine the phase and structure of ZnSe films. Fig 1 shows the XRD spectra of as deposited 200 nmZnSe films deposited on to the quartz substrates and annealed at 200°C and 300°C. The structure of all the three film shows a single peak corresponding to cubic ZnSe phase. The peak is noted at value of 20 at 27.47corresponding to (111)plane of cubic ZnSe as confirmed from JCPDS X-ray powder file data⁷. The full width at half maximum (FWHM) of the cubic (111) peaks were calculated and was found to decrease with increasing annealing temperature. The decrease in FWHM could be attributed to decrease in the concentration of lattice imperfection as the micro-strain decreases within the film and the crystallite size increases. The grain size is calculated using Debye Scherrer formula for crystallite size $D = (0.94 \lambda/\beta \cos \theta)$ where β is the full width half maxima in radians, λ is the wavelength of X-rays. The grain size is found to be 30 nm, 32 nm and 37 nm for as deposited film and films annealed at 200°C and 300°C respectively. It is noted that the grain size increases with increasing annealing temperature.



Fig 1: XRD spectra of post deposition annealed ZnSe films

Raman Spectroscopy Analysis

Fig. 2 shows first-order Raman spectra of as deposited ZnSe thin films and films annealed at 200°C and 300°C. There are two main Raman active modes observed at 205cm⁻¹ and 250 cm⁻¹⁸. The peaks observed for the as deposited film at 207.94 cm⁻¹ and 253.34 cm⁻¹ correspond to the TO and LO mode respectively. For the film annealed at 200°C, the TO and LO mode were observed at 210.95 cm⁻¹ and 252.09 cm⁻¹ respectively. The film

which was annealed at 300°C, the TO and LO modes were observed at 206.68 cm⁻¹ and 252.09 cm⁻¹⁹. Also a

small peak at 500 cm⁻¹ is observed in the Raman spectra of all four films, which is attributed to second order LO mode¹⁰. Raman spectra shows that there is no increase in crystalline nature of the film annealed at 200°C as its intensity almost matches with that of the as deposited filmbut for the film annealed at 300°C, its crystalline nature increases profoundly which can be seen with the sharp rise in the intensity of Raman spectra of the film annealed at 300°C.



Fig 1: Raman spectra of ZnSe films

UV Vis spectroscopy Analysis

The absorption spectrum is studied using the UV –Vis Spectroscopy. The band gap is determined using absorption spectrum. In semiconductor nanoparticles, the effective band gap increases with the decreasing particle size of nanoparticle and the absorption edge shows a blueshift¹⁰. For direct transition band gap is calculated by plotting (α)² versus E_{phot}(eV) where α is the absorption co-efficient, h is the Planck's constant, v is the light frequency and E_{phot} is the photon energy in eV. The value of E_{phot} extrapolated to α =0 gives an absorption energy, which corresponds to the band gap E_g¹¹. The band gap calculated using the above relation for as deposited film and films annealed at 100°C and 200°C is found to be 2.65eV , 2.72eV and 2.75 eV respectively. An increase in band gap or the blueshift of 0.05eV is observed which is attributed to size quantization leading to quantum confinement of the nanostructures¹².



Fig 3: Band gap calculation of ZnSe films

Conclusions

ZnSe thin films annealed in argon atmosphere at 200°C and 300°C are studied. The peaks corresponding to (111) plane of ZnSe shows increase in the grain size due to annealing. The Raman spectra also reveals peaks corresponding to LO and TO mode of ZnSe and the intensity is found to increase with annealing temperature which confirms that the crystalline nature of the film increases with annealing temperature. The optical studies reveal band gap corresponding to ZnSe with quantum confinement effect manifested by the blue shift of the films with increasing annealing temperature.

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