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FORMATION OF ZnSe BY STACKED ELEMENTAL LAYER METHOD

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Zn-Se bilayer thin films have been deposited on well cleaned glass substrate by using the vacuum evaporation technique under a vacuum of 5×10^{-5} Torr. These bilayer thin films were modified by ion irradiation, vacuum annealing and rapid thermal annealing. X-ray diffraction and optical measurement of as deposited and modified samples have been performed. The formation of cubic ZnSe phase has been observed in modified samples and optical band gap value has been found to be in the range of ZnSe compound.

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1. Introduction

ZnSe is a II-VI compound semiconductor with a direct optical band gap of 2.7 eV at room temperature [1], which makes it suitable material for a variety of the optoelectronic applications in the blue green wave length region, including light emitting diodes and lasers [2]. It is also used as window material in high efficiency solar cells, because its large band gap permits a large number of photons to reach the absorber layer [3]. The fabrication of general electronics and optoelectronics devices requires both n and p type materials, ZnSe has been found in both n and p type conduction [1]. ZnSe is the first choice for high power laser windows.

For deposition of ZnSe thin films several techniques have been reviewed: Electrodeposition [4], Photochemical deposition [5], Vacuum evaporation [6], and Pulsed laser deposition [7]. These conventional techniques have some disadvantages, for example during vacuum thermal evaporation of ZnSe the composition of the film may be changed. A well-defined composition of Zn-Se can be formed in thin film form by stacked elemental layer (SEL) [8] deposition and their intermixing.

The stacked elemental layer deposition method has been used for CdTe by Curz and de Avillez [8] and copper indium diselenide thin film by Carter et al. [9]. It is particularly suitable for deposition of compound semiconductor thin films, as it provides good control of composition. This method has been used as a promising method for producing highly efficient CdTe/CdS solar cells as reported by Ohshita [10]. Thermal annealing and ion irradiation can perform the mixing of bilayer.

The present work deals with the study of Zn-Se bilayer deposition of and then mixing of bilayer by ion irradiation and annealing to form the ZnSe compound and characterization by XRD and optical reflection spectra.

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2. Experimental procedure

Zn-Se bilayer thin films have been prepared by vacuum thermal evaporation at pressure 10^{-5} torr in HIND HI VACCUM system. The high purity Zn (99.99%, shots-1-2 mm size) and Se (99.99+%, pellets< 4mm) placed in two different boats in vacuum system. The glass substrate was placed in the substrate holder above the boats carrying the materials. The Zn layer was first deposited and later Se layer deposited to get bilayer of Zn-Se system. In order to get the desired stoichiometry, the thickness of elemental layers must be adjusted; for a ZnSe film. The number of atoms in Zn and Se layers must be identical; this leads to the following relation-ship between thickness of elemental layers: t_{Se}/t_{Zn}= 1.78. In present work, we have deposited 140 nm and 250 nm thickness of Zn and Se respectively. For mixing of these bilayers three different methods such as vacuum annealing, rapid thermal annealing and SHI irradiation have been used. For vacuum thermal annealing we have placed the radiation heater inside the vacuum chamber and put the sample over it. The radiation heater takes 10 minutes to raise the temperature from room temperature to 373K. The sample then annealed at this constant temperature 373K for one an hour. Similarly these samples were also annealed at 413K and 443K for one an hour. The rapid thermal annealing has been performed by 1000 W halogen lamp for 20 sec. Swift heavy ion irradiation was carried out at Inter University Accelerator Center (IUAC), New Delhi using 15 UD Pelletron facilities. Material science beam line was used for irradiation of the samples. The vacuum in the target chamber is generally maintained up to 10^{-6} torr. The samples have been mounted on the ladder which have four faces and can slide vertically and rotate also (clock & anticlockwise). The samples were irradiated uniformly at room temperature over an area of 1cm x 1cm by scanning the ion beam with electronic magnetic scanner. The Ni^{+7} ion beam of 100 MeV energy with beam current 1.5 pnA at the fluences of $1x10^{13}$ ions/cm^2 have been used for irradiation. The angle of incident during the irradiation was normal with respect to the sample. The reflectance spectra of as deposited and three different treated samples recorded in 380-800 nm range using Hittachi-330 spectrophotometer. The X-ray diffraction of these samples were also performed using Cu-Kα (λ=1.5406 Å) radiation.

3. Results and discussion

Figure 1, shows X-ray diffraction patterns of as deposited, vacuum annealed, rapid thermal annealed and ion irradiated (1×10^{13} ions/cm^2) Zn-Se bilayer thin films (1400-2500 Å). It has been observed that as deposited sample shows only elemental peaks of Zn and Se, while treated samples shows Zn and Se peaks and ZnSe compound peaks and intensity of elemental peaks reduced. The XRD analysis was done by Powder-X software and lattice parameter are in good agreement with JCPDS data. ZnSe phase appeared in vacuum annealed (443 K) bilayer films, at $2\theta = 39.08^o$ (JCPDS Card: 37-1463) along (211) plane. Similarly in rapid thermal annealed and ion irradiated bilayer thin films ZnSe phase appears. It indicates the bilayer mixing by vacuum thermal annealing, rapid thermal annealing and ion irradiation. From XRD results it is observed that peak intensity for ZnSe phase has been found to be increased in ion irradiation, as compared to vacuum thermal annealed and rapid thermal annealed as shown in Figure 2. This indicates that mixing at interface due to vacuum thermal annealing and rapid thermal annealing is partial as compared to ion irradiation. Similar results have been observed by Mangal et al [11] in case of Al-Sb bilayer mixing by vacuum thermal annealing and rapid thermal annealing. Dhuri et al [12] has been observed mixing in Fe/Si multilayer by ion irradiation and vacuum thermal annealing and observed that ion irradiation gives better mixing.

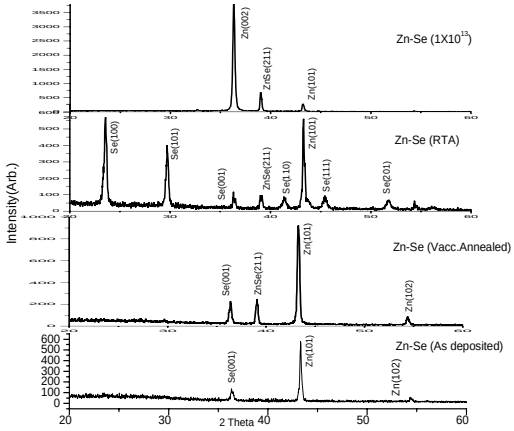

Fig. 1. X-ray diffraction patterns for as deposited, vacuum annealed, rapid thermal annealed and ion irradiated (1×10^{13} ions/cm^2) Zn-Se bilayer thin films (1400-2500 Å).

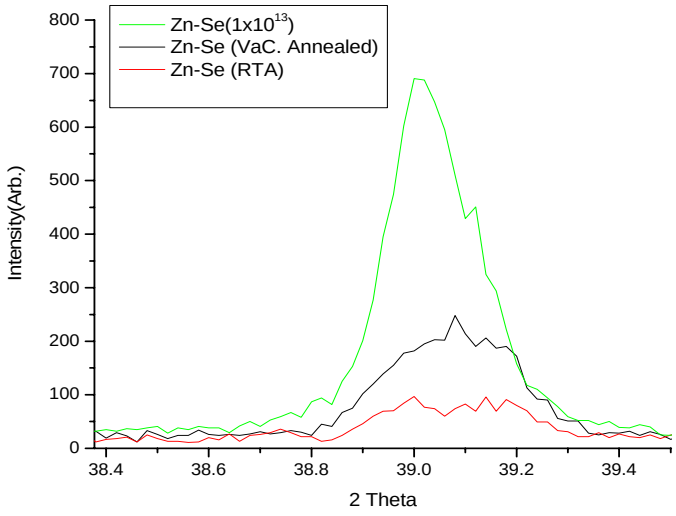

Fig. 2. X-ray diffraction peak correspond to ZnSe in vacuum thermal annealed, rapid thermal annealed and ion irradiated Zn-Se bilayer thin films (1400-2500 Å).

One can compare relative effect of vacuum thermal annealing (VTA), rapid thermal annealing (RTA) and swift heavy ion (SHI) irradiation in Zn-Se as follows.

1. Rapid thermal annealing (RTA) is very effective for crystallization of Se along with partial mixing at the interface.
2. Vacuum thermal annealing only enhances the Znse formation at the interface. There is no enhancement in crystallization of Se and Zn.
3. Swift heavy ion (SHI) irradiation favors the Zn crystallization along with ZnSe formation. The selenium crystallization is not effective.

The reflection spectra of as deposited and treated by three different methods recorded as deposited sample does not show any sharp absorption edge but treated samples shows absorption edge as shown in figure 3.

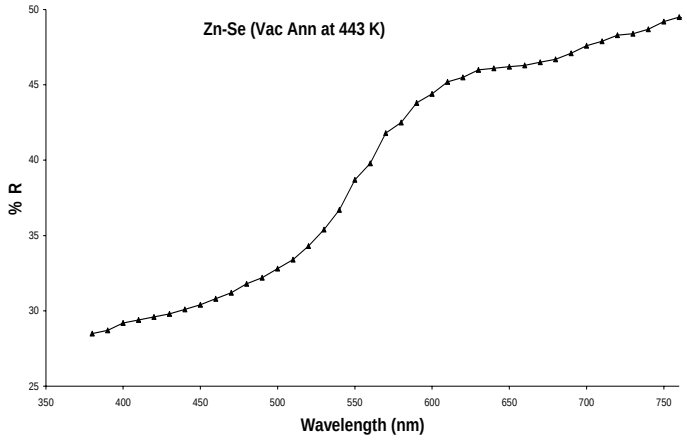

Fig. 3. Optical reflection spectra of vacuum thermal annealed Zn-Se bilayer thin film (1400-2500 Å).

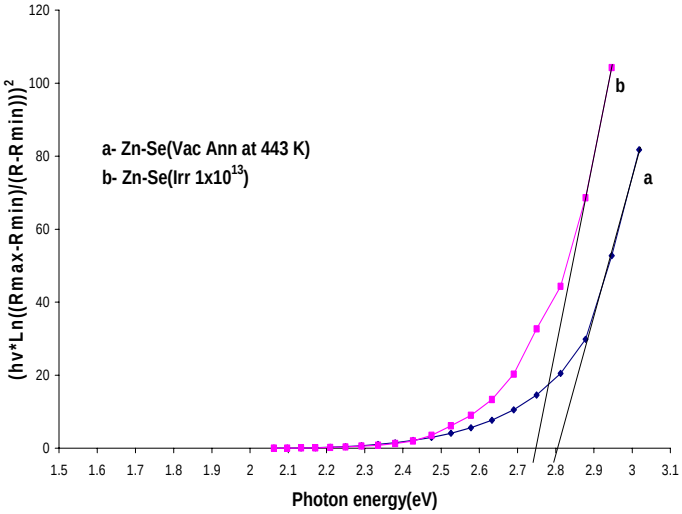

Fig. 4. Optical band gap of vacuum thermal annealed and ion irradiated Zn-Se bilayer thin films (1400-2500 Å)

The optical band gap of the treated samples (vacuum annealed and ion irradiated) calculated by reflectance methods [13], by plotting the graph between $[h\nu * \ln(Rmax-Rmin)/(R-Rmin)]^2$ and hν (as abscissa), where Rmax and Rmin are the maximum and minimum values of reflectance and R is the reflectance for various values of λ in the reflectance spectra's straight line is observed and extrapolation gives the values of direct band gap. We found that band gap for SHI irradiated sample is 2.74 eV and Vacuum annealed sample is 2.80 as shown in figure 4. Variation of optical band gap with different treatments and thickness are shown in table 1.

Table 1. Variation of optical band gap with different treatments.

Sample	Band gap (eV)		
	Ion irradiated	Vacuum annealed	Rapid thermal ann.
Zn-Se	2.74	2.80	2.82

It indicates that ion beam mixing, gives better mixing than vacuum thermal annealing and rapid thermal annealing process. Optical measurements confirm the bilayer mixing and better mixing have been observed in ion irradiation.

Similar results also observed by Mangal et al [14,15], in case of Al-Sb bilayer mixing and mixing can be achieved by ion irradiation, vacuum thermal annealing and rapid thermal annealing, and better mixing can be achieved by ion irradiation.

Ion beam mixing explained by Kraft et al. [16] using thermal spike model (TSM). Thermal spike assumes that the energy deposited initially in the electronic subsystem in 10^{-15}–10^{-14} s gets subsequently transferred to the atomic subsystem via electron-phonon (e-ph) coupling in 10^{-13}–10^{-12} s. Depending on the material and the energy deposited by ion surrounding of the ion path may significantly exceeds the melting point and a liquid cylinder of some nm in diameter is formed, which subsequently quenched to the ambient temperature within a few tens to a hundreds of ps. Due to high cooling rate, a nonequibilirum material is left in the ion track. Such a transient increase of temperature within a very small local volume is often called a "thermal spike". This mechanism should results in atomic transport across the interface of a high energy ion bombarded layer system.

Mixing by vacuum thermal annealing and rapid thermal annealing can be explained by diffusion process at interface by Charter et al [9] and Niscomb et al [17]. In diffusion the interface couples usually a region of high defect concentration, which influences the nature of phase evolution under heat treatment. The defect evaluation at the interface itself depends on the components. Enhanced diffusion of one component in a bilayer thin film across the interfaces can leave behind a large vacancy concentration. A large symmetry in the diffusion rate results in the production of a strong counter flux of vacancy defects, which under certain conditions agglomerate to form voids called Kirkendall voids /Newcomb et al. [17]/. The isothermal heat treatment of the bilayer results in the inter diffusion and reaction between the elements accomplished by the consequent nucleation and growth Charter et al [9]

Raghavan et al. [18] has explained on the basis of secondary ion mass spectrometry (SIMS) and low energy positron beam (LEPB) in case of Al/Ge bilayer that there is no inter diffusion in the as grown sample. After annealing at 370 K, little inter mixing is observed. As the annealing temperature is increased beyond 370 K, substantial inter diffusion is observed. As the annealing temperature is increased, most of the Ge segregates to the near-surface regions.

4. Conclusion

It is concluded from the above study that ZnSe can be prepared by using bilayer deposition of Zn and Se thin films using different mixing techniques such as SHI irradiation, Vacuum annealing (VA) and Rapid thermal annealing (RTA). The XRD and optical study confirms the formation of ZnSe compounds at the interface.

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