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OPTICAL CONSTANTS OF CO-EVAPORATED Ag_2Se THIN FILMS WITH PROTON IRRADIATION

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Polycrystalline Ag_2Se thin films have been prepared by co-evaporation of individual elements on glass substrate at a high temperature. The samples were subjected to the irradiation of 1.26 M eV protons (H^+). The effect of irradiation on the structural and optical properties has been investigated for different doses of H^+ ions. The optical band gap energy is found to vary significantly with H^+ irradiation dose. The crystallinity of the films found to increase with small doses and decrease with higher irradiation dose.

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1. Introduction

Silver Selenide is an interesting material, which belongs to the group of superionic conductors. As for all other silver chalcogenides, this compound undergoes a first order polymorphic phase transition around 400 K. The low temperature polymorph is a semiconductor of low band gap. Silver selenide has been used as thermochromic material for non-linear optical devices, rechargeable secondary batteries and multipurpose ion-selective electrodes. It is a well known fact that silver selenide undergoes a polymorphic phase transition. Many researchers have reported different values for this transition temperature. Das and Karunakaran [1] reported the thickness dependence of transition temperature and activation energy. The low temperature phase below 400 K was identified as β-Ag_2Se with an orthorhombic structure and the high temperature α-Ag_2Se with bcc structure. According to Abdullayev et al. [2], silver selenide exists as a high temperature cubic phase (α) and low temperature orthorhombic (β) and tetragonal phase with transition temperature of about 408 K or 395 K. Moreover the β-α transition does not occur directly but through an intermediate phase; the extension of this new phase increases from cycle to cycle. The structural data available in literature are contrary for the low temperature phase. The compound has been described as tetragonal, orthorhombic and monoclinic by different authors. Ridder and Amelincks [3] have listed different structural parameters reported by different researchers.

Many methods have been used for the preparation of silver selenide thin films, which include vacuum evaporation [1], explosive evaporation [2], flash evaporation [4], chemical bath deposition [5], sequential evaporation [6-8], and conversion of Ag films by chemical method [9]. In the present work Ag_2Se thin films were prepared by reactive evaporation technique. The as prepared films are subjected to 1.26 MeV H^+ irradiation and the variation of structural and optical properties are investigated and reported for the first time.

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2. Experimental

Co-evaporation technique is employed for the preparation of silver selenide thin films. Co-evaporation or reactive evaporation, a variant of the Gunther`s three temperature method for the preparation of compound thin films [10]. Cleaned glass substrates were used for the preparation. High purity silver (99.999%) and selenium (99.99%) were utilised for evaporation. Silver was evaporated from molybdenum boat and selenium from a glass crucible kept in a molybdenum basket. The glass substrates were mounted on a substrate holder with a heating arrangement and temperature was measured with the help of a fine wire chromel-alumel thermocouple. The temperature of the substrate was maintained at 398±5K throughout the deposition. The rate of deposition and substrate temperature were optimised by trial and error. The optimization of the preparation conditions of indium selenide thin films are reported elsewhere [11]. The film thickness were measured using the well known Tolansky`s multiple beam interferometric technique. The thickness of the films used for the present studies is approximately 200 nm.

Proton irradiation was carried out at 3.0 MV tandom pelletron accelerator, at ion beam laboratory, Institute of Physics, Bhubaneswar, India. 1.26 MeV ion beam was used for the irradiation. The irradiation was done at 1×10^{14}, 5×10^{14} and 1×10^{15} ions/cm^2 with approximate beam current of 30 nA. The irradiation is carried out with a beam size of 1 cm X 0.5 cm and the samples are mounted perpendicular to the beam. XRD spectra were recorded using Rigaku D-Max C XRD unit. Optical transmittance and reflectance were recorded using Hitachi 3410 UV-Vis-NIR spectrophotometer.

3. Results and discussion

3.1 Energy loss and ion range

As the bombarded high energy ions penetrate in to a solid target, they slow down due to the interaction with the solid target and finally come to rest at a depth normally referred to as the range. As an ion penetrates a solid, it loses its energy by inelastic electronic excitations as well as by elastic collisions with atoms. The former process is referred to as electronic loss (S_e) and the latter process is known as nuclear stopping (S_n). The ion range, electronic loss and nuclear stopping are calculated using TRIM (Transport of ions in matter) code [12]. The range, S_e and S_n at 1.26 MeV for Ag_2Se is 12.4 μm, 0.84 keV/nm and 6.57×10^{-4} keV/nm respectively. Since the ion range is very high compared to the film thickness (0.2 μm), the effects, which are discussed here, would be mainly due to the defects produced by the irradiation of H^+

3.2 Structural studies

The most accepted crystal structure of low temperature Ag_2Se is orthorhombic with the $P2_12_12_1$ space group. Fig. 1 shows the X-ray diffraction pattern of a typical silver selenide thin film prepared at a substrate temperature of 398 K. This indicates the existence of (002), (004) and (014) planes of reflections of orthorhombic phase of silver selenide, which are in good agreement with JCPDS card no. 24-1041. This indicates that the crystallites have a mixed orientation. The lattice parameters were calculated and its values are a = 4.353 Å, b = 6.929 Å and c = 7.805 Å.

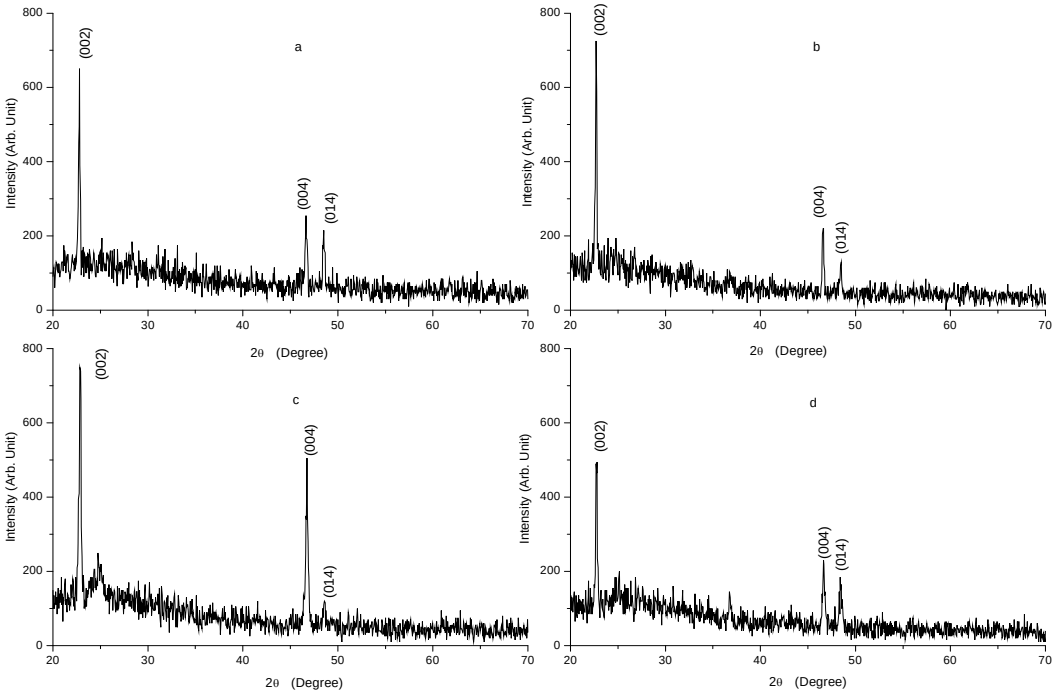

Fig. 1. XRD pattern of proton irradiated Ag_2Se thin films a) as-prepared b) Dose = $1X10^{14}$ ions/cm^2 c) Dose = $5X10^{14}$ ions/cm^2 d) Dose = $1X10^{15}$ ions/cm^2

It is observed that the intensity of XRD peak increases with H^+ irradiation dose and decreases slightly for the dose of 1×10^{15} ions/cm^2. This behaviour is similar to the work we reported earlier [13] for evaporated silver indium selenide films. The ion irradiation and energy depositions process can be explained on the basis of thermal spike model [14]. According to this model, deposited energy produces secondary electrons along the path of the ion track. The secondary electrons those have higher energy move away from the ion track by leaving a row of positively charge ions. The electrons with lower energy transfer their energy and come in equilibrium within 10^{-15} s. This energy is transferred to the atomic lattice by electron–phonon coupling that can induce a local temperature rise along the track. The local rise in temperature in a very short span of time induces crystallization in the material. Since, the total amount of energy deposited into the lattice increases with ion fluency, hence the degree of crystallinity also increases resulting in the increase of XRD peak intensities [15].

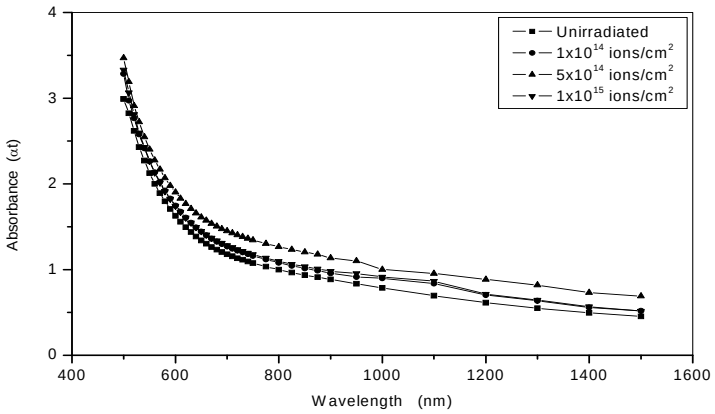

Fig. 2. Absorption spectra of Ag_2Se thin films with different proton doses.

It is however, interesting to observe that, at the fluency of $1x10^{15}$ ions/cm^2 intensities of all XRD peaks reduce. This indicates a decrease in crystallinity that could originate from either the ion beam generated defects and dislocations [16, 17], or the grain splitting effect [18] at high fluency; which dominates over the thermal spike induced crystallization process.

3.3 Optical properties

Since the presence of defects and irradiation induced disorder significantly affect the optical properties, optical absorption spectrometry is an ideal technique for investigating the effect of irradiation in semiconductor thin films. However there is no published work available on optical properties of ion implanted or irradiated Ag_2Se thin films. The absorption coefficient (α) is calculated from the transmission and reflection data using the following relation:

$$\alpha = \frac{1}{t}\ln\left(\frac{1-R}{T}\right) \tag{1}$$

where t is the film thickness, R is reflectance and T is the transmittance. Figure 2 shows the absorption coefficient versus wavelength plot of un-irradiated and H^+ irradiated Ag_2Se thin films.

In the high absorption region Tauc [19] and Davis and Mott [20] showed that the absorption coefficient (α) and photon energy ($h\nu$) are related by the equation.

$$\alpha h\nu = A(h\nu - E_g)^n \tag{2}$$

where A is a constant and E_g is the band gap of the material and n has values 1/2, 3/2, 2 and 3 depending on the optical absorption process. n = 1/2 can be the best fit here. Plotting $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$), and extrapolating the linear portion of the curve to absorption equal to zero, gives the value of the direct band gap (E_g). Figure 3 shows $(\alpha h\nu)^2$ vs $h\nu$ plot of $AgInSe_2$ thin films with different proton doses. This gives band gap energy of 1.580 eV, which is a direct allowed one for unirradiated samples. The band gap was found to decrease from 1.580 eV, for as prepared samples, to 1.519 eV for a proton dose of 5×10^{14} ions/cm^2 and increase slightly to 1.554 eV with a dose of 1×10^{15} ions/cm^2. This variation in optical band gap can be understood from the variation in structural properties explained earlier. As the crystallinity increases the band

gap found to decrease to the bulk value but at higher proton dose the crystallinity of the films decreases and consequently optical band gap found to shift to higher side.

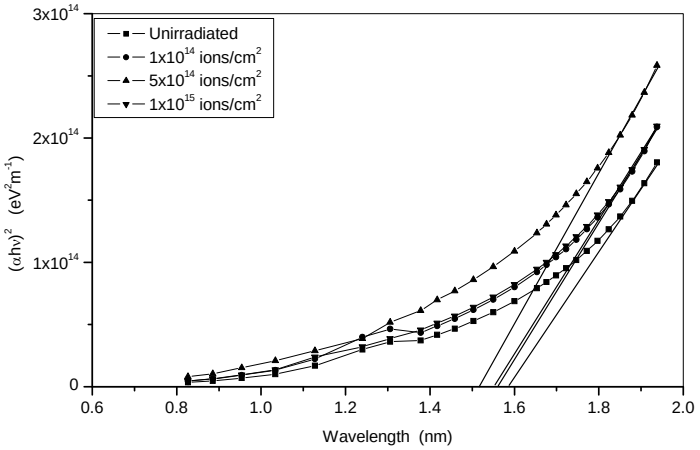

Fig. 3. $(\alpha h\nu)^2$ vs $h\nu$ plot of Ag_2Se thin films with different proton doses

The extinction coefficient (k) was calculated using the relation $\alpha = 4\pi k/\lambda$ and refractive index n by the relation

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{3}$$

where R is the reflectance. Figure 4 shows the refractive index variation with wavelength at various proton doses. The refractive index is found to increase with dose, attain a maximum at $5x10^{14}$ ions/cm^2 and then decreases.

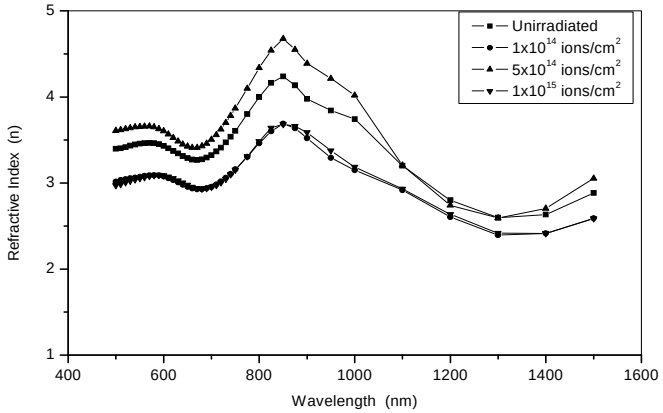

Fig. 4. Refractive index (n) versus wavelength with proton dose.

The sharpness of the band edge is another parameter, which is significantly affected by irradiation-induced disorder. To understand the effect of irradiation on the crystallinity of the films, the Urbach [21] relation was used to compute the width of band tail states. The width of band tail can be estimated by the relation

$$\alpha = \alpha_0 \exp\left(h\nu / E_0\right) \tag{4}$$

where α_0 is a constant and E_0 the band tail width. The reciprocal of the slope of $\ln(\alpha)$ versus $h\nu$ plot give the width of band tail. The band tail is found to increase gradually up to 5×10^{14} ions/cm^2 and decrease slightly for higher dose. The band gap and band tail variation is given in Table 1. The observed increase in E_0 suggests that the variation in band gap as a result of irradiation is predominantly due to lattice disorder produced during irradiation.

Table 1. Band gap and band tail variation of proton irradiated Ag_2Se thin films.

Sample	Band gap (eV)	Band tail (eV)
Un irradiated	1.580	0.980
1×10^{14} ions/cm^2	1.561	0.982
5×10^{14} ions/cm^2	1.519	1.177
1×10^{15} ions/cm^2	1.554	1.025

4. Conclusions

Silver selenide thin films were prepared by vacuum co-evaporation of individual elements. The H^+ irradiation is found to affect the optical properties of the films. The optical band gap energy is found to vary significantly with H^+ irradiation dose. The crystallinity of the films found to increase small doses and decrease with higher irradiation dose. This is because of irradiation induced crystallization and defects formation the films with various doses.

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