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200 MeV Ag^+ ION BEAM INDUCED MODIFICATIONS IN $AgInSe_2$ FILMS DEPOSITED BY HOT WALL VACUUM EVAPORATION METHOD

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We prepared $AgInSe_2$ films by hot wall technique on glass substrate at 135°C using the stochiometric powder. The films were characterized by X ray diffraction and UV-vis-NIR spectroscopy. The samples were subjected to 200 MeV Ag^+ ion beam irradiation with dose rage 5×10^{10} - 1×10^{12} ions/cm^2. Samples show complete transition from crystalline to amorphous state upon irradiation. The band gap energy estimated for as deposited and irradiated films is found to decrease upon irradiation. Pristine samples show two band edges at 1.19 and 2.09 eV, which are due to the fundamental absorption edge and transition originating from crystal field splitting respectively. The effect of irradiation on optical properties has been investigated for different doses of ion. It is observed that after ion irradiation the band gap values of silver indium selenide films corresponding to fundamental absorption edge and the transition due to crystal field splitting decrease to 1.15 and 1.56 eV respectively, which may be due to irradiation induced defects. Conductivity and mobility decreases with the silver ion fluency however carrier concentration show slight increase in its value.

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1. Introduction

The modification of thin film properties by high-energy particle (electron, proton, γ-rays) and swift heavy ion (SHI) irradiation has gained much attention in recent years due to several aspects like a consequence of future technological requirements to form buried layers with modified properties [1], to determine the stability of devices made for space applications [2] and also to produce nanostructures by SHI irradiation [3,4].The irradiation of materials with energetic radiations and ions leads to the creation of a wide variety of defect states in the material system, which changes the physical and chemical properties such as structure, optical and electrical transport properties of the material. The changes are strongly dependent on the mass of the incident ion, the energy and fluence. The irradiation may cause ionization or excitation and possibly displacement of atoms from their sites in the lattice of the materials, which results to new electronic configuration and coordinates modifies the optical properties of the films [5]. $AgInSe_2$ is a member of the I-III-VI_2 group of semiconductors. In recent years, the ternary chalcopyrite

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semiconductors have been receiving considerable attention because of their adaptability, as an absorber component, in thin film solar cells. The I-III-VI_2 compounds are the ternary analogues of II-VI compounds. $AgInSe_2$ is a ternary analogue of CdSe, which has been used for a number of electronic devices. $AgInSe_2$ is a semiconductor with energy gap of 1.20 eV . They crystallize in the chalcopyrite structure, which is closely related to zinc blend structure. $AgInSe_2$ crystallizes into chalcopyrite structure with the c/a ratio approximately equal to 2 .Ternary chalcopyrite compounds have photovoltaic potential for solar cells since their optical band gap lies between 0.8 and 2.0 eV . Ramesh et al observed an efficiency of 7.5 % for p-$AgInSe_2$/ n-CdS solar cell in which $AgInSe_2$ is used as absorber material [6].Recently 9 % conversion efficiency has been reported by Mustafa et.al. for device prepared on n-type Si with laser ablation [7]. $AgInSe_2$ belongs to this group of compounds and is a promising material in optical applications because it has a direct band gap, high optical absorption (10^{-5} cm^{-1}), capability of p and n-control, and with relatively high mobility [8-10]. All of these characteristics are better than those of $CuInGaSe_2$ [11,12] for solar cell applications which is being used as 19.9 % efficient device [13]. However, there are only few reports which address AIS as compared to CIS. The commonly used methods for preparing silver indium selenide thin films are flash evaporation [14], rf magnetron sputtering [15], thermal evaporation [16,17], solution growth technique [18] , hot press [19], hot wall [20] and pulse laser ablation [21].Optical properties of single-crystalline chalcopyrite semiconductor $AgInSe_2$ has also been studied by spectroscopic ellipsometry (SE), and photo reflectance (PR) spectroscopy [22] In the present work we employ hot wall evaporation technique in high vacuum. The objective of the present work is to investigate the effect of 200 M eV irradiation on the properties of Silver indium selenide films grown at low Ts by hot wall method.

Whenever an energetic ion passes through a medium it causes noticeable changes in it. Depending upon the material (insulator, conducting or semi conducting), ion energy and type different types of modifications are expected. Energy loss during ion passage from the medium can be described via two independent processes, viz., ion {atomic nucleus interaction that dominates at low energies (»0.1 MeV/amu) and ion {electron interaction prevalent at high energy for heavy ions. Thermal spike [23] and Coulomb explosion [24] models have been proposed to describe the conversion mechanism for the energy of the excited electrons into the kinetic energy of the target atoms. The former model assumes the excited electrons to be confined in a cylinder around the ion path.. 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. A few reports are available of proton and He^+ irradiation effect on AIS [25,26].

2. Experimental

Bulk silver indium selenide was prepared by fusing the stochiometric composition of individual elements in a quartz ampoule. The quartz ampoule was evacuated to 10^{-3} mbar and sealed. This is then fired to a temperature of 1173 K by increasing the temperature in steps of 200 K. The ampoule is kept at the temperature for 48 h and cooled slowly to room temperature. The ampoule is carefully cut and the silver indium selenide is powdered. The details of preparations of films by hot wall method are described in earlier published work [27]. The temperature of the substrate was maintained at 135^0C throughout the deposition. XRD spectra were recorded Bruker X ray diffractrometer. UV–vis–NIR spectrophotometer Perkin (elmer) was used for optical studies. 200 M eV SHI irradiation was carried out at 15 UD tandom pelletron accelerator, Inter University accelerator center New Delhi , India. with irradiation dose at 5 X 10^{10} ,1 X 10^{11} , 5 X 10^{11} , 1 X 10^{12} ions/cm^2 . Later the effect of swift heavy ion on the structural, optical and electrical properties was studied. The electrical measurements were carried out by Vander Pauw method with programmable keithley electrometer (6517A) and a constant current source. Indium was used as ohmic contacts. To avoid contaminations, the measurements were performed in a vacuum system at a pressure of 10^{-3} mill bars using a conductivity cell in the temperature range 300–400K. The electromagnet that produces a field up to 0.6T using dc power supply was used for hall measurements at room temperature using the Van der Pauw method for electrical characterization like mobility and carrier concentration. Optical absorption spectra of the AIS films irradiated with 200 M eV silver beam was recorded using Perkin-Elmer UV-VIS-NIR spectrometer. XRD scan of the films were taken using Cu Kα (wavelength =1.5405 A^0) radiations in 2θ range 20^0-80^0 by Bruker diffractrometer.

3. Result and discussion.

Fig. 1 shows the XRD patterns of $AgInSe_2$ films deposited by hot wall vaccum evaporation method. The XRD results are in conformity with JCPDS card of $AgInSe_2$ [JCPDS-00-035-01099]. The structural analysis of as-deposited and 200 MeV Ag^+ ion irradiated films were performed using XRD technique. In the XRD spectra, as shown in Fig. 1, we observed that the pristine sample showed a strong texturing along with (112) peak at 25.6^0 being the preferential orientation. The XRD patterns of non-irradiated sample exhibit peaks due to the (112) only, suggesting the growth of single phase material. The lattice parameters so calculated have been found to be c = 11.60 Å and a = 6.10 Å, which are very close to the reported values [6,16] showing tertragonally distorted structure of hot wall grown AIS films. Also, the c/a ratio was found to 1.90 Å which is less than 2. These observations are in good agreement with those of Santhosh et al. [26] for chalcopyrite films. The XRD patterns of samples irradiated with silver swift heavy ion with different doses is shown in Fig. 2 .First fluency value 5 X 10^{10} ion/cm^2 is sufficient to damage the (112) chalcopyrite phase and seems threshold for its damage. It results in phases corresponding to $AgIn_5Se_8$ (121) [4] and orthorhombic phases [28], which further disappear with higher doses .It is observed that samples have damaged completely after irradiation with swift heavy ion with fluency more than 5 X 10^{10} ion/cm^2.The sudden decrease in intensity could be attributed to the creation of defects such as ion tracks and crystalline to amorphous transition. The ion tracks were created from the ion-induced melt due to the mechanical stress arising from the thermal expansion [29].The possible explanation for this kind of structural modification induced by SHI irradiation can be explained by total energy deposited in electronic excitations/ ionizations in the films by energetic ions. The imparted energy of the incoming ions in our films at different fluence increase the strain between the grains in the films and it results in further decrease in the crystalline quality of the film. We suppose that the lattice vibrations induced by ions in single tracks increase the interfacial energy between AIS grains and promote a lattice disordering inside large grains. It is worth noting here, that SHI irradiation induced disordering is reported earlier in various systems of chalcopyrite and other inorganic semiconductors [29,30]

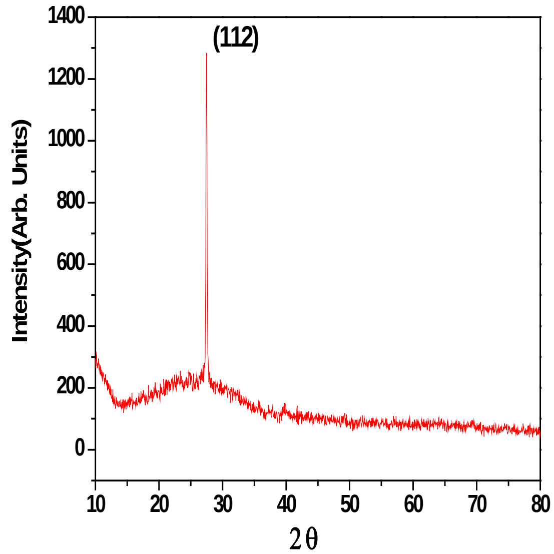

Fig 1 , XRD pattern of AIS films grown on glass by hot wall vacuum evaporation method

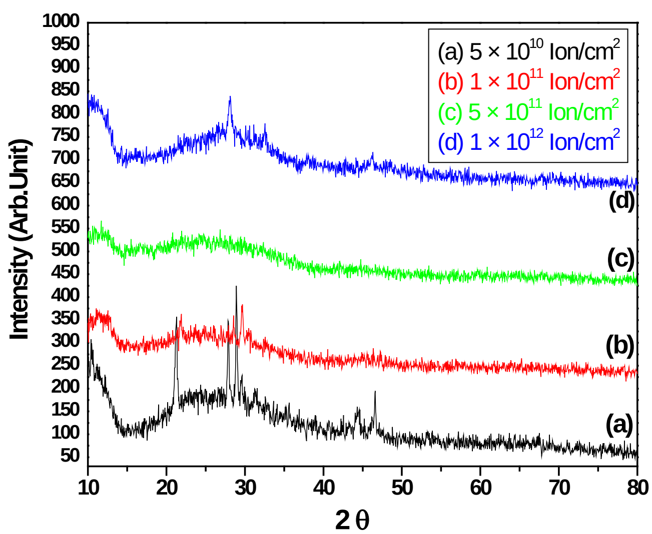

Fig 2 , XRD pattern of hot wall grown AIS films irradiated with 200 M eV silver ion with dose range 5 X 10^{10} - 1 X 10^{12} ions/cm^2

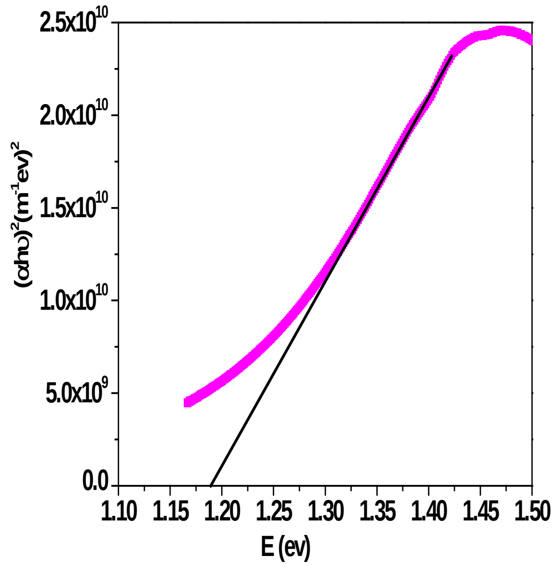

Fig 3 , Variation of absorption coefficient with E (eV) (for first edge)

The optical studies were carried out on the silver indium selenide thin films prepared by hot wall evaporation of the powder $AgInSe_2$. Optical transmission spectra of the as prepared as well as the SHI irradiated samples were recorded from 200 to 1100 nm. Fig. 4 shows the variation of optical absorption of heavy ion irradiated silver indium selenide thin films with the as prepared sample of thickness 1.5 µm. The optical band gap energies were calculated using the equation [31]

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^{1/2}$$

where Eg is the band gap, α is the absorption coefficient, υ is the frequency, A is a constant and n can have values 1/2, 3/2, 2 and 3 depending up on the mode of inter band transition i.e. direct allowed, direct forbidden, indirect allowed and indirect forbidden transition respectively. n = 1/2 offer the best fit for the optical absorption data of silver indium selenide thin films. In order to evaluate the optical band gap, $(\alpha h\nu)^2$ versus hν plot is made, which is shown in Fig. 3. It is observed that the band gap of silver indium selenide thin films decreases gradually with silver swift heavy ion fluencies [Fig 4 and 6]. The as deposited sample has a band gap of 1.19 eV, which decreased to 1.15 eV and 2.09 eV [Fig 5] to 1.56 eV for transition due to fundamental absorption edge and transitions originating from crystal field splitting respectively at a fluency range of 5×10^{10} ,1×10^{11} , 5×10^{11} , 1×10^{12} ions/cm^2 . This variation in optical band gap can be understood from the variation in structural properties explained earlier. Band Gap value has decreased due to disorder in structure with irradiation and fluence. It is also observed that the effect of swift heavy ion irradiation on optical transition due to crystal field splitting are more pronounced as compared to those transitions which arises due to fundamental absorption edge.

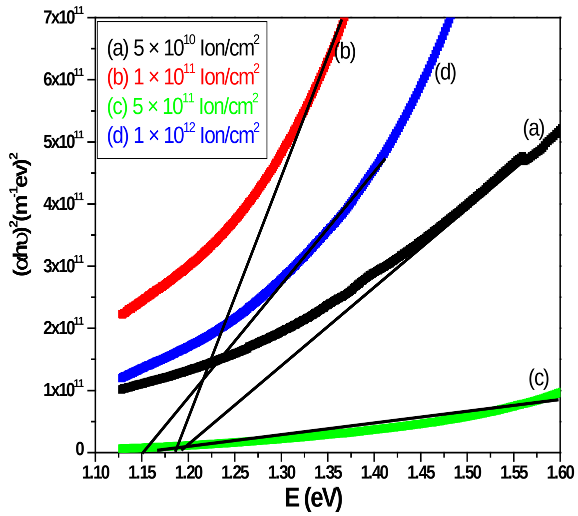

Fig 4 , Variation of absorption coefficient with E (eV) for different doses of silver ion beam (for first edge).

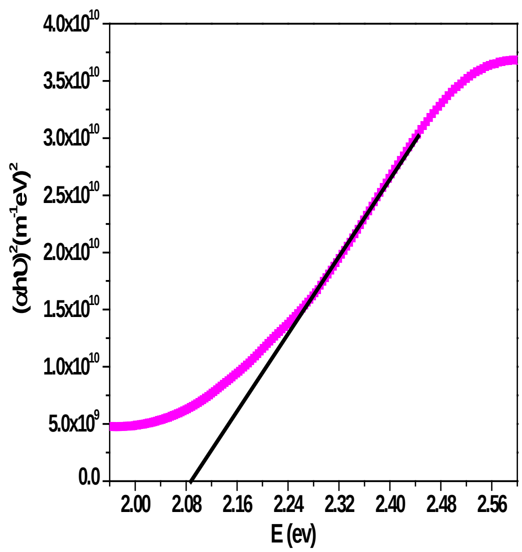

Fig 5 , Variation of absorption coefficient with E (eV) (for second edge).

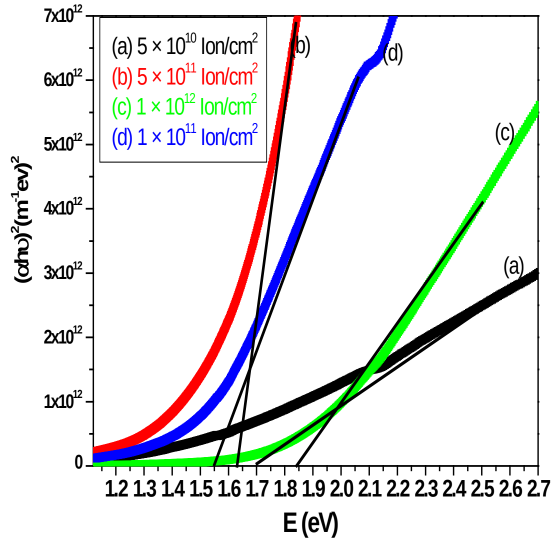

Fig 6 , Variation of absorption coefficient with E (eV) for different doses of silver ion beam (for second edge).

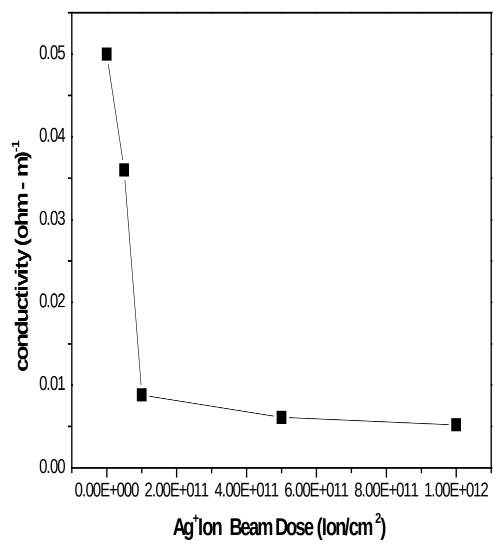

Fig 7 , Variation of room temperature conductivity with different doses of silver ion Beam.

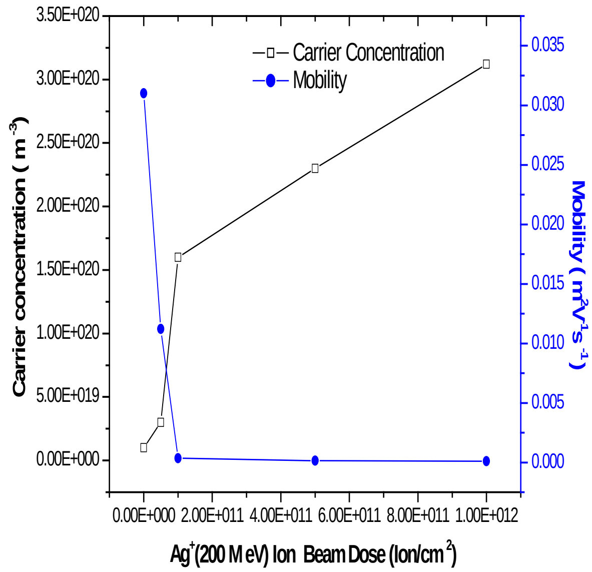

Fig 8, Variation of mobility and carrier concentration with different doses of silver ion Beam.

Fig 7 show the variation in conductivity at room temperature as a function of silver swift heavy ion fluence. The pristine samples has conductivity 0.050 $(\text{Ohm-m})^{-1}$ at room temperature .The conductivity decreases with silver ion dose, This can be understood by considering the crystalline to amorphous transition by irradiation. Samples have damaged by 200 M eV. silver ion beam and hence the damaged samples show high resistivity due to dominant role of grain boundaries. Also similar trend has been observed for mobility. Due to damage of crystalline network with ion irradiation the boundary influence the movement of charge carrier and hence show decreasing trends [Fig 8]. As far as the carrier concentration is concerned it has shown very slight enhancement which may be due to the Ag/In vacancies.

4. Conclusion

$AgInSe_2$ films were grown on glass by hot wall vacuum evaporation method. The grown samples were irradiated with 200 M eV silver swift heavy ion with fluence range 5 X 10^{10} - 1 X 10^{12} ions/cm^2 at room temperature .SHI induced disordering is observed after irradiation of this chalcopyrite system . Samples show transformation from single phase to complete amorphous state .Decrease in optical transition edges has also been observed which is explained due to increase in defects. Irradiated samples show decrease in conductivity, mobility and a small increase in carrier concentration which is explained due to disorder and Ag/In vacancy. It is proposed that for tuning the properties of hot wall deposited $AgInSe_2$ films by SHI irradiation the samples should be irradiated with low fluence and low energy in order to avoid complete damage of lattice structure.

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