STRUCTURAL AND ELECTRICAL PROPERTIES OF HIGH ENERGY ION BEAM AG IRRADIATED IN/SE BILAYER

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Abstract

In the present work In(~50nm) over Se (~50nm) thin films were deposited successively on the Si substrate by e-beam evaporation method under 2×10^{-5} mbar pressure. The In/Se bilayers were irradiated with beam of 100 MeV Ag^{+7} with fluence of 1.5×10^{13} ions/cm^2. The sample was then characterised by XRD for phase formation and Rutherford backscattering spectrometry (RBS) for thickness profile. XRD revealed phase formation in Pristine sample thereby confirming mixing. RBS also confirms mixing in Pristine sample. SEM analysis shows the formation of stone like nanostructures in Pristine sample with varying sizes. These nanostructures size are affected by Ag ion irradiation. Other electrical measurements like resistivity and Seebeck coefficient of Pristine and Irradiated samples with temperature were also carried out. Irradiated sample shows much improved Seebeck coefficient in comparison to Pristine sample at room temperature. Hall effect measurement was also done to know the concentration and type of charge carriers in both samples. Pristine sample shows n type charge carriers whereas Ag irradiated sample shows p type charge carriers. Resistivity of Pristine sample shows semiconductor behaviour with increase in temperature. But with Ag irradiation its value falls to half at room temperature. Pristine sample structural and electrical properties were compared with Ag ion irradiated sample.
Key words: Indium Selenide, ion beam mixing, RBS, Seebeck coefficient, XRD, Hall measurement, resistivity.

Introduction:

The need for clean energy in this world is increasing very high due to adverse effects of using Petroleum products. In near future we will be left with no Petroleum. So, we have to look for the alternative sources of energy of which use of thermoelectric material is one of the solutions. Thermoelectric device work on the principle of Seebeck effect in which if two dissimilar metals are joined together end to end to form a loop and if a temperature difference is maintained at

two junctions, current starts to flow. This current can be used to power electrical appliances at lower scale. So, there is a need to synthesize thermoelectric materials with higher efficiency. The efficiency of the thermoelectric material is given by dimensionless quantity known as figure of merit ZT,

$$ZT = \frac{S^2 \sigma T}{k}$$

Where S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature in kelvin and κ is the thermal conductivity of the material. κ is made up of two parts κ_e (electronic part) and κ_p (phonon part) and $\kappa = \kappa_e + \kappa_p$.

ZT can be increased either by increasing σ or by decreasing κ. But they are related to each other by Weidmann-Fanz law

$$\frac{\kappa_e}{\sigma} = L \cdot T$$

Where L is known as Lorentz factor having value $2.44 \times 10^{-8} W\Omega K^{-2}$. Now since heat conduction takes place both by electrons and phonons and electrons are the fundamental particles of all materials which can not be altered. Only option left is to creat phonon scattering centre to depress thermal conductivity thereby ZT can be increased. The ion beam processing is one of the unique ways of fabrication of thin films and has been used recently for thermoelectric thin films. These ion beam synthesized thermoelectric films were shown to be nanostructured having higher Seebeck coefficient [1,2].

Indium Selenide is one of the important materials of III-VI group of the periodic table. It exists in different phases - InSe, In_2Se_3, In_4Se_3, In_4Se_5 and In_6Se_7. Indium-Selenium based alloy thin films have wide range of applications like solar energy conversion [3], diode formation [4], infrared device fabrication, laser making [5] and thermoelectric devices [6].

The ion beam processing of materials is one of the attractive ways of synthesis of thin films and has been used recently for synthesis of thermoelectric thin films [7]. Ju-Hyuk et al [8] showed that $In_4Se_{2.35}$ gives best thermoelectric performance (ZT=1.48 at 705K) among all In-Se compound In_4Se_3, and $In_4Se_{2.35}$ prepared by mechanical alloying. Ion beam mixing technique is used to produce defects at the boundary of bilayer of Indium and Selenium. These defects serve as the phonon scattering centres, thereby increases the thermoelectric figure of merit of the sample.

Swift Heavy Ions (SHI) transfer their energy mainly by inelastic collisions (electronic energy loss, Se) which can create point defects [9], columnar defects or perturbed atomic distribution [10]. The nuclear energy loss in this case is negligible. At certain threshold Se, the incident ions can induce atomic displacement in the target materials. Hence mixing can take place in layered system [11,12]. Defects can also be produced by SHI radiation at the interface [13]. And after rearrangement of the interfacial atoms, it can cause mixing of the two layers.

In our work, compound formation, electrical and structural in Pristine and Ag ion irradiated Indium- Selenium thin films were studied.

Experimental procedure:
The samples were deposited Indium over Selenium by using e beam evaporation vacuum coating unit BC-300 available at MNIT, Jaipur on Si substrate under the pressure of 2×10^{-5}

mm Hg. The high purity Indium (99.9%) 300 mesh and high purity Selenium (99.5%) powder were obtained from Alfa Aesar, USA. These films were irradiated by Ag^{+7} ions with fluence 1.5×10^{13} ions/cm^2 and energy 100 MeV at 15 UD Pelletron IUAC, NEW DELHI. XRD of the pristine and irradiated samples were carried out by PANalytical X'Pert assembly available at MRC, MNIT, Jaipur. This facility offers CuKα x-rays of wavelength 1.540 A^o. The angle of incidence of the x rays was varied from 10° to 80°. RBS of pristine and irradiated samples were carried out in Pelletron Accelerator RBS-AMS Systems (PARAS) located at IUAC, NEW DELHI.   He^{2+} ions with energy 1.7 MeV were used to obtain the RBS spectra. RBS data confirms the mixing of Indium and Selenium at pristine state. SEM of pristine and irradiated sample were carried out by SEM which is a field-emission scanning electron microscope (FE-SEM) situated at IUAC, New Delhi. The electrical characterisation like Hall measurement, Resistivity and Seebeck were also carried out at IUAC, New Delhi.

Results and discussion
XRD, RBS and SEM analysis
The electronic energy loss Se of Ag ion is calculated using TRIM [14] is 1.774 KeV/A^o for Indium with projected range 10.41μm and 1.333 KeV/A^o for Selenium with projected range 13.95 μm. The structural composition of the grown films was studied through XRD. The Pristine sample was marked as In/Se/P and Ag irradiated sample as In/Se/1.5e13Ag. Figure 1 shows the XRD of Pristine and Ag irradiated samples.
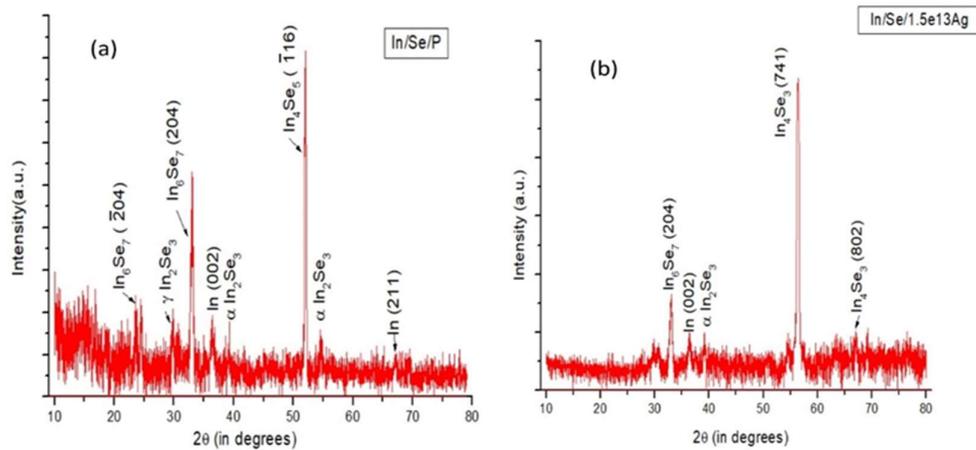
Fig 1 (a) XRD of Pristine sample and (b) Ag irradiated sample at fluence 1.5×10^{13} ions/cm^2

The XRD (fig 1a) of the Pristine sample confirms mixing and revealed compounds of Indium Selenium with presence of $In_6Se_7(2\overline{0}4)$, $In_6Se_7(204)$ in Monoclinic phases, $In_4Se_5(1\overline{1}6)$ in monoclinic phases, unreacted pure Indium in tetragonal BCC structure along the phases In (002) and In (211), αIn_2Se_3 and γIn_2Se_3. As per XRUMP simulations and depth profile of Pristine sample (fig 2 a, b) the top layer shows a thickness of 10 nm pure indium and second layer of 40 nm thick with Indium-Selenium intermixed. Selenium in the third layer has a part of Indium from second layer with total thickness 65 nm and substrate Silicon in the fourth layer has little Selenium mixed from third layer with thickness 7 nm.
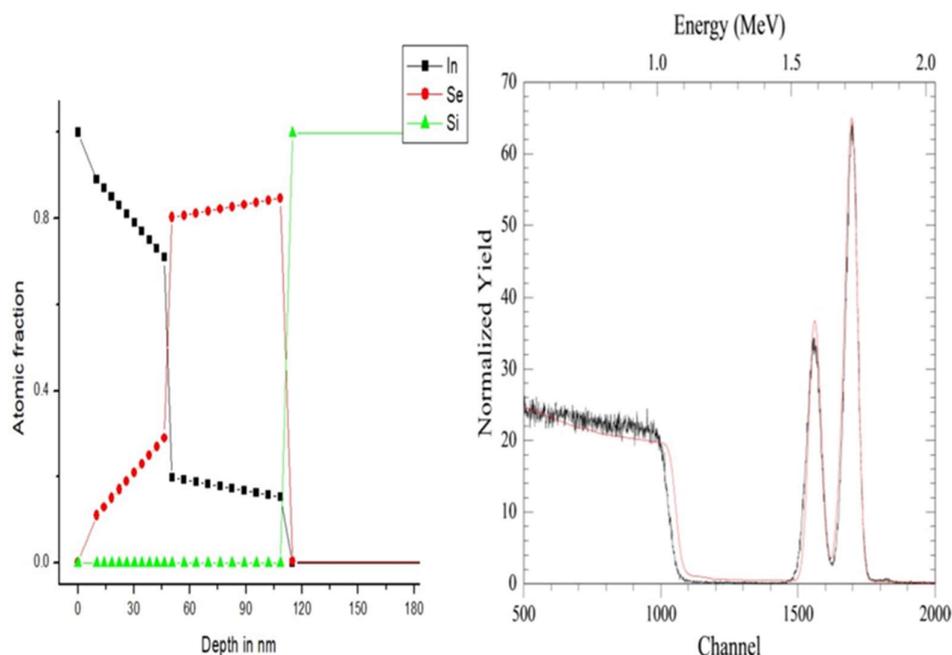
Fig 2 (a) Depth profile and (b) RBS Spectra of Pristine In/Se sample

With the irradiation of Ag^{+7} ions with fluence 1.5×10^{13} ions/cm^2 and energy 100 MeV, most of Indium reacted with Selenium and new phases like orthorhombic $In_4Se_3(741)$ and $In_4Se_3(802)$ are formed and the growth of $In_6Se_7(204)$ and αIn_2Se_3 are seen. The following figures (fig 3 a,b) shows the SEM images of Pristine and Ag ion irradiated samples. The SEM of Pristine sample reveals stone like nano structures. The average size of the nanostructures is calculated by using Scherrer equation:

$\tau = \frac{0.9\lambda}{FWHM \cdot cos}$ where τ is the mean size of crystallites domain, λ is wavelength of X-rays used, FWHM= Full Width at half Maxima and θ is the Bragg's angle of the corresponding peak. For Pristine sample, average particle size is 7 to 20 nm, whereas for Ag ion irradiated sample average particle size is 9 to 20 nm. As can be seen from fig 4 b, with the irradiation of Pristine sample with Ag ion, there is a mixing on the surface and stone like nanostructures are not prominent, as they got mixed up.
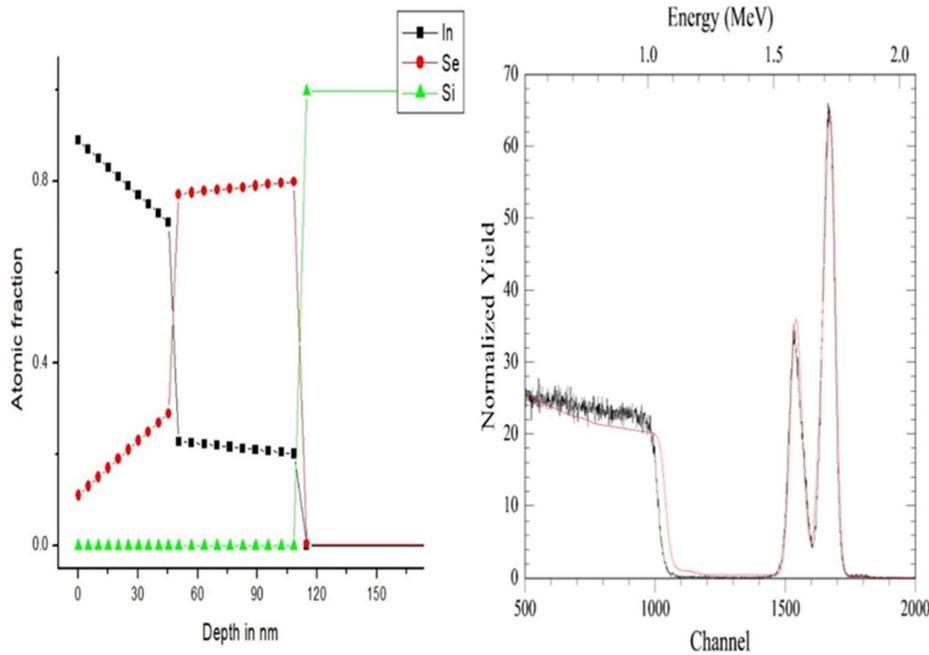
Fig 3 (a) Depth profile and (b) RBS Spectra of Ag irradiated In/Se sample

As per XRUMP simulation and depth profile of Ag irradiated sample, the first layer has Indium Selenium intermixed layer with thickness 50 nm and second layer 65 nm. Third layer has a width of 7 nm with Selenium and Silicon intermixed and not much affected by irradiation.
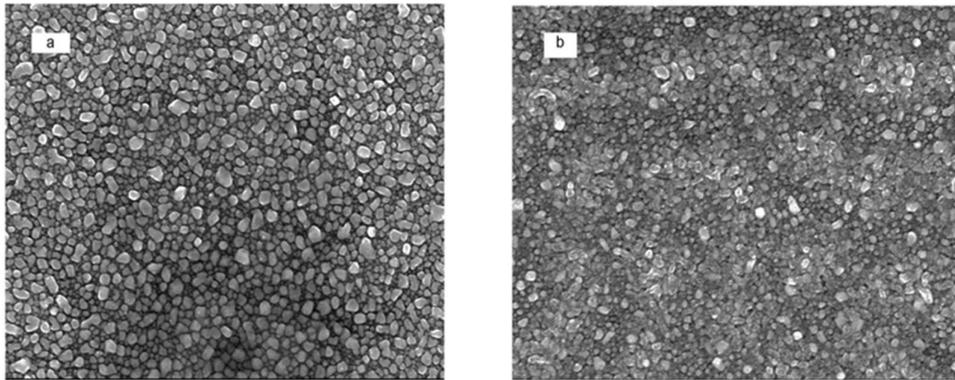
Fig 4 . SEM images of (a) Pristine (b) Ag ion irradited samples

Seebeck, Resistivity, Power factor and Hall analysis

The Pristine sample has n type carriers with avearge Hall coefficeint, Carrier concentration and mobility : 0.02195 cm^3/C, 2.843×10^{20} /cm^3 and 0.2102 cm^2/Vs respectivly. The variation of Seebeck coefficient with temperature for Pristine sample is shown in the fig 5a. Seebeck coefficient has value about 2.23 µV/K at 300 K. From 300 K to 409 K there is a gradual increase in value of Seebeck coefficient,but after 409 K there is sharp increase. Its value is 120 µV/K at 420K.This may be due to mixing of two layers of Indium and Selenium at higher temperature and formation of other compounds of Inidum-Selenium. The resisitivity (fig 5b) of Pristine sample shows semiconductor behavior as it falls of with rise in temperature. At 300 K, it has resistivity of   2.05×10^{-3} Ωcm and power factor 2.78 µW/m/K^2 (fig 5c).   With

increase in temperature, resistivity decreased and power factor increased. At 420 K resistivity of Pristine sample is 1.68×10^{-3} Ωcm, Seebeck coefficient and Power factor are 120μV/K and 864 μW/m/K^2 respectively.

Fig 5(a) Seebeck Coefficient variation with Temp. (b) Resistivity variation with Temp. (c) Power factor vaiation with Temp. for Pristine sample

With irradiation of Pristine sample with Ag ions of 100 MeV at fluence 1.5×10^{13} ions/cm^2, sample has p type carriers with avearge Hall coefficeint, Carrier concentration and mobility of 0.1186 cm^3/C, 5.261×10^{20} /cm^3 and 0.444 cm^2/Vs respectivly. The resistivity of the sample falls to half (fig 6b) i.e., about 1.08×10^{-3} Ωcm at 300 K in comparison to Pristine sample. At 300 K Seebeck coefficient also showed a very high value to about 26 μV/K (fig 6a) which is nearly 12 times more than that of Pristine Seebeck coefficient value at same temperature. Moreover, Power factor value also increased from 0.28 μW/m/K^2 in Pristine to 68.5 μW/m/K^2 in Ag irradiated sample at 300 K which is very high increment. Power factor increased with increasing temperature and has highest value 3687 μW/m/K^2 at 385 K, after which it falls off gradually. With increase in temperature Seebeck coefficient increased and at 385 K, highest Seebeck coefficient for irradiated sample is observed which is about 109 μV/K, and then falls of with increase in temperature. The resisitivity of Ag irradiated sample also shows a semiconductor behavior as it shows a sharp fall with increase in temperature.
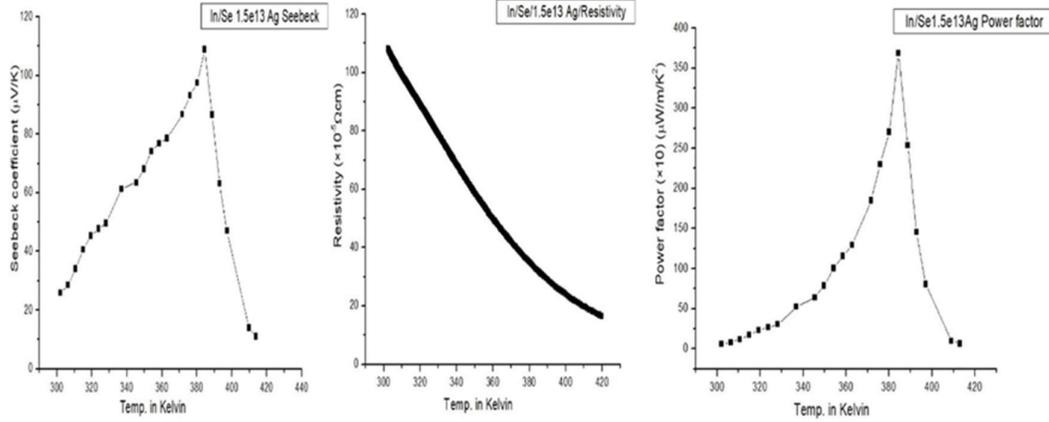
Fig6 (a) Seebeck Coefficient variation with Temp. (b) Resistivity variation with Temp. (c) Power factor variation with Temp. for Ag irradiated In/Se sample

Conclusions:

o   The Pristine sample is good thermoelectric material at temperature from 400 K onward.

o   Ion beam irradiation can be used to prepare In/Se samples, as in our case Ag ion irradiation has increased Seebeck and Power factor values many folds.

Acknowledgements:

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