

INFLUENCE OF INDIUM DOPING ON THE OPTOSTRUCTURAL AND MORPHOLOGICAL PROPERTIES OF CHEMICALLY DEPOSITED MoBi_2Se_5 MIXED METAL-CHALCOGINIDE THIN FILMS

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Indium doped MoBi_2Se_5 thin films were prepared by using simple arrested precipitation technique (APT). The precursors used were molybdenum, bismuth, indium triethanolamine complexes along with organic additives. Ammonium molybdate, Bismuth nitrate, Indium sulphate and sodium selenosulphite were used as sources of Mo^{4+} , Bi^{3+} , In^{3+} and Se^{2-} respectively. The growth mechanism of thin film formation, composition, microstructure and electrical properties of these films were studied by UV-Visible NIR Spectrophotometer, X-ray diffractometer (XRD), Energy dispersive X-ray analysis (EDAX), Atomic Force Microscopy (AFM), scanning electron microscope (SEM), Electrical conductivity and Thermo-electric power measurement (TEP). The effect of bath composition, substrate temperature, deposition time, pH and rate of agitation on morphology of Indium doped MoBi_2Se_5 thin films were investigated. The XRD results showed that, Indium doped MoBi_2Se_5 are polycrystalline in nature. Optical study revealed that, In doped MoBi_2Se_5 thin films is a direct gap semiconductor material having band gap energy in the range 1.78 eV to 1.47 eV. The linear variation of the plot confirms the semiconducting nature of the material. TEP study of In doped MoBi_2Se_5 thin films shows that material is n type semiconductor and applicable for solar cells.

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1. Introduction

Ternary and quaternary chalcogenide alloys have attracted much interest in recent years due to their wide range applications including photovoltaic and phase change optical storage media [1-4]. Also In doped MoBi_2Se_5 thin films of ternary and In doped MoBi_2Se_5 thin films of quaternary chalcogenide semiconductors are leading candidates among photovoltaic materials mainly because they have a wider range of optical and electrical properties than elemental materials and its alloys find many applications such as in small scale thermoelectric power generator, optical recording materials, thermoelectric cooler thermopile, thermoelectric refrigerator materials [5-8]. It is observed that In doped MoBi_2Se_5 thin films are good candidates for phase change optical media and the amorphous phase of these films is stable. Their optical properties remain unaffected by normal environmental conditions. Recently, intensive efforts have been carried out in pursuit of improved phase change characteristic and device performance. Doping has been one of the effective means of tuning the alloys phase change properties. Although variety of dopants including gallium, indium, arsenic and selenium [3, 9-15] has been utilized and detailed understanding of the effects of some dopants is still lacking. Especially, we believe that indium effects on the phase change characteristic have not been clarified due to the phase segregation problem caused during sample preparation. Various methods have been used for preparation of quaternary thin films such as CVD, MOCVD, CBD, spray pyrolysis, electro deposition, sputtering,

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MBE, etc [16-20]. However none of the method has been entirely satisfactory when considered from production perspective. Therefore it is likely to develop a hybrid deposition technology that is the combination of chemical bath deposition and controlled precipitation method. Among all these technique arrested precipitation technique is well known technique also this technique has many advantages such as simpler, low cost and in APT wastage of material is minimum [21,22,23].

There is no any single report for In doped MoBi_2Se_5 thin films preparation. Also there is no reports available on the preparation of In doped MoBi_2Se_5 thin films by chemical bath deposition or any another method. In the present investigation efforts are made to synthesize In doped MoBi_2Se_5 thin films of various chemical composition, to optimize the preparative parameters for obtaining high-quality and well reproductive In doped MoBi_2Se_5 thin films. Solar cell is a recent research and development area for fabrications higher efficiency solar cells by arrested precipitation technique. In this communication we report results on optical, structural, morphological and electrical properties of the In doped MoBi_2Se_5 thin films.

2. Experimental details

2.1. Preparation of In doped MoBi_2Se_5 thin films.

Indium doped MoBi_2Se_5 thin films have been prepared by an arrested precipitation technique by allowing the Mo-TEA, Bi-TEA, In- TEA complex to react with Se^{2-} ions, which are released slowly by the dissociation of Na_2SeSO_3 in alkaline medium at pH 9.5 Ammonia solution was used to adjust pH of reaction mixture. To study the effect of indium doping on optostructural, morphological and electrical properties of In doped MoBi_2Se_5 thin films amount of In varied from 0.0 ml to 1.0 ml. All the chemicals used were of AR grade. Microglass slides of dimensions 75 mm \times 25 mm \times 1.35 mm were used as substrates. The substrates were cleaned well subsequently using chromic acid, detergent, distilled water and then dried prior to film deposition. Thoroughly cleaned glass substrates were mounted on a specially designed substrate holder. The substrate holder was attached to constant speed gear motor. The parameters such as deposition time (90 min.), temperature of deposition bath (75°C) and speed of substrate rotation (45 rpm) were optimized. After deposition, samples were taken out, washed with distilled water and kept in dark desiccators.

2.2. Characterization of the sample

After synthesizing the thin films their optical, structural, morphological and electrical characterizations were performed. The optical study was performed in the range of wavelength between 350 to 850 nm using Uv-Vis-NIR spectrophotometer (Hitachi model 330, Japan) at room temperature. X- ray diffraction (XRD) analysis was carried out using a Philips PW-1710 X-ray diffractometer for the 2θ ranging from 0° to 100° with Cr K_α line used as a target ($\lambda=2.289\text{\AA}$). The thickness of film was determined by surface profiler (AMBIOS XP-1).

The electrical conductivity of the films was studied by using two point D. C. probe method. As the contact resistance of the film is very low compared to film resistance, the two probe method is accurate and hence used for electrical conductance measurements. The area of the film was defined and silver paste was applied to ensure good electrical contact to the films. The working temperature was recorded using a Chromel-Alumel thermocouple. The potential drop across the film was measured with the help of Meeco 801 digital multimeter and current passed through the sample was noted with a sensitive 4 digit picoammeter (Scientific equipment, Roorkee DPM 111).The measurements were carried out by keeping the film system in a light tight box, which was kept at room temperature.

Thermoelectric power measurement was carried out under the condition of maximum temperature difference and minimum contact resistance to decide the type of semiconductivity. The thermoelectric voltage was measured with digital Testronix micro voltmeter. A JEOL-JSM-6360A electron microscope with an energy dispersive X-ray analysis (EDS) attachment is used to

record the scanning electron micrograph (SEM), Atomic Force Microscopy (AFM) and EDS spectrum of the sample.

3. Results and discussion

3.1 Growth Mechanism

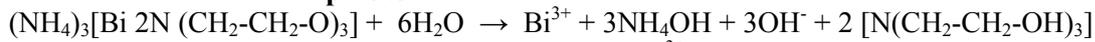
In alkaline medium Mo-TEA complex slowly releases Mo^{4+} ions at 9.5 pH [24-25].

pH 9.5



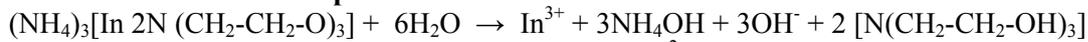
In alkaline medium Bi-TEA complex slowly releases Bi^{3+} ions at 9.5 pH

pH 9.5

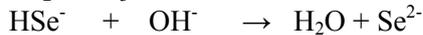


In alkaline medium In-TEA complex slowly releases In^{3+} ions at 9.5 pH

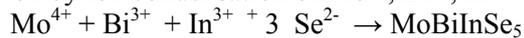
pH 9.5



Na_2SeSO_3 dissociates in alkaline medium to produce Se^{2-} ions



Ion by ion condensation of Mo^{4+} , Bi^{3+} , In^{3+} and Se^{2-} results in



3.2. Optical analysis

Optical absorbance measurement of the film was used to estimate the band gap energy from the position of absorption edge. Optical absorption coefficient (α) of the material is of the order of 10^4 cm^{-1} . Near the absorption edge α is given by [26, 27]

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

Where A is an energy dependant constant, $\text{h}\nu$ is photon energy and $n=1/2$ for direct band gap materials. The optical absorption data was used to plot a graph of $(\alpha\text{h}\nu)^2$ vs. $\text{h}\nu$. The plot of $(\alpha\text{h}\nu)^2$ vs. $\text{h}\nu$ yielded straight line at higher energies indicating direct type of transition. Extrapolation of the plot to the x-axis gives the energy band gap of the deposited film as shown in figure 1. The band gap determined from $(\alpha\text{h}\nu)^2$ vs. $\text{h}\nu$ plots is found to be 1.78 eV to 1.47 eV. It was found that the optical energy gap decreases gradually with increasing indium mole content [0.0 to 1.0] as shown in Table 1. The decreasing band gap is related with partial size from XRD data and SEM [28, 29].

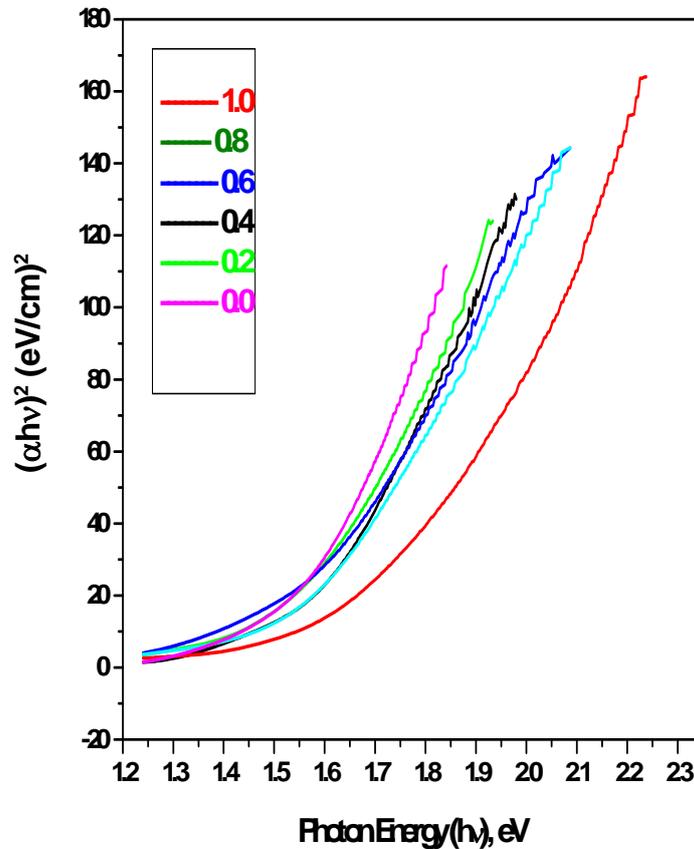


Fig. 1. The $(\alpha h\nu)^2$ vs. $h\nu$ plots for the In doped MoBi_2Se_5 thin films having different composition.

3.3 XRD analysis

Figure 2 shows the XRD pattern of MoBi_2Se_5 and In doped MoBi_2Se_5 thin films having different composition ($x = 0.0$ ml, 0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml, 1.0 ml) deposited at 45°C . The peaks become broader and some peaks appeared at high θ values with increasing In doping. The deposited layers exhibited polycrystalline nature which is explained by the presence of (221) and (130) peaks. The plane indices are obtained by comparing the intensities and positions of the peaks with JCPDS data. There are no JCPDS standard data available for different composition of In doped MoBi_2Se_5 . Hence the plane indices are obtained by comparing the intensities and positions of the peaks with those of MoSe_2 , Bi_2Se_3 and In_2Se_3 which are given by JCPDS file no. 77-1715, 81-0834, 71-0521, 72-2123, 77-2016, 72-2182, 81-0834, 40-0908 and 24-0772 as shown in Table 2. The formation of solid solution is expected because both materials crystallises in orthorhombic structure. This small degree of broadening occurs as a result of increase in strain in the film due to In incorporation in the Bi lattice site. This indicates that the crystal quality decreases with an increase of indium content in the films.

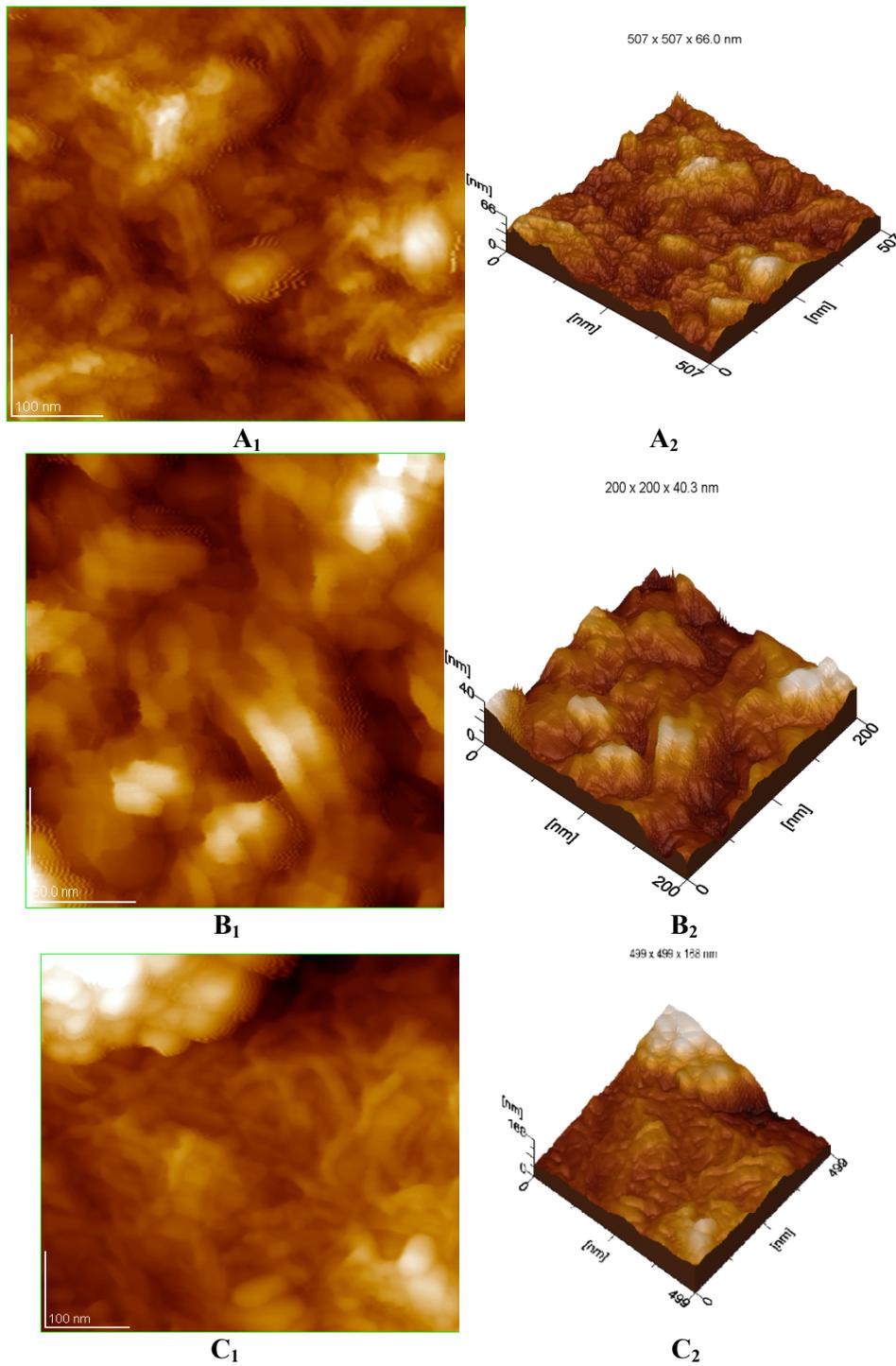


Fig. 2. XRD for the In doped MoBi_2Se_5 thin films having different composition. (a) $x_1 = 0.0$ (b) $x_2 = 0.2$ (c) $x_3 = 0.4$ (d) $x_4 = 0.6$ (e) $x_5 = 0.8$ (f) $x_6 = 1.0$

The crystallite size of the film is calculated using Scherrer formula [30] crystallite size $(D) = 0.9 \lambda / \beta \cos \theta$

Where,

λ is the wavelength of the X-ray radiation used

β is the full width at half maxima

θ is Bragg's angle

The crystallite size calculated for the In doped MoBi_2Se_5 thin films having different composition. (a) $x_1 = 0.0\text{ml}$ (b) $x_2 = 0.2\text{ ml}$ (c) $x_3 = 0.4\text{ ml}$ (d) $x_4 = 0.6\text{ ml}$ (e) $x_5 = 0.8\text{ ml}$ (f) $x_6 = 1.0\text{ ml}$ reflection is 47.7, 44.4, 40.1, 37.3, 33.5, 35.8 nm with increasing In doping respectively.

3.4. AFM analysis:-

Figure 3 (A_1, A_2, A_3) and (B_1, B_2, B_3) shows 2D and 3D AFM images of samples In doped MoBi_2Se_5 thin films respectively. A quantitative method to examine the surface morphology and structure is obtained by analyzing the surface roughness using AFM. Figure 3 shows the Spherical and fibrous shaped grains uniformly grown over the surface of the substrate. Which is favorable for the conduction hence material is suitable for the fabrication of solar cells.

All the results obtained from AFM data are consistent with scanning electron microscopy (SEM) results.

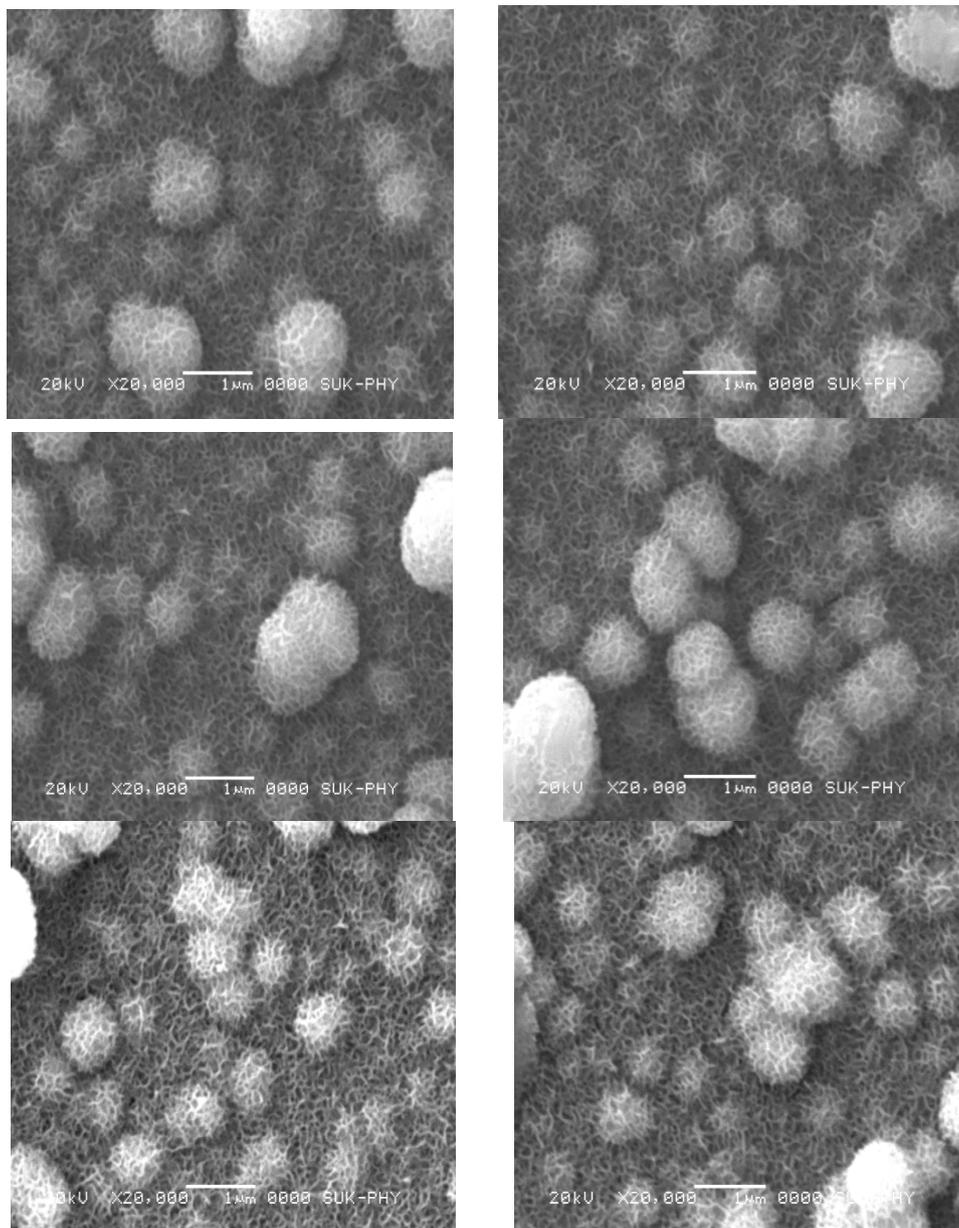
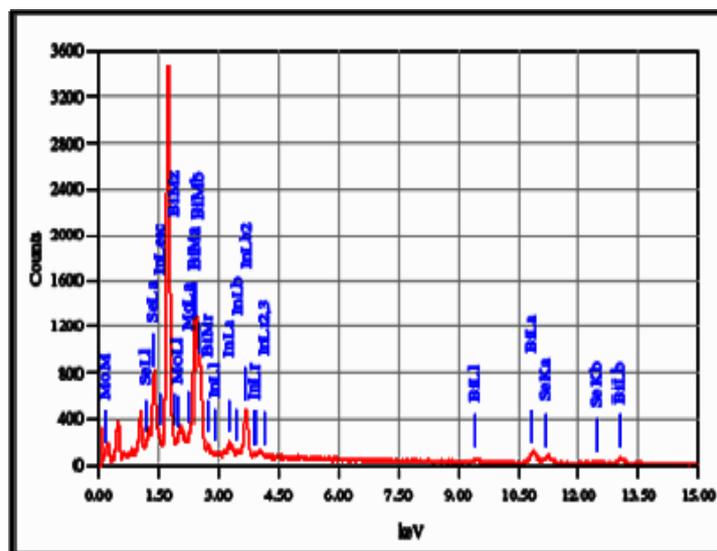


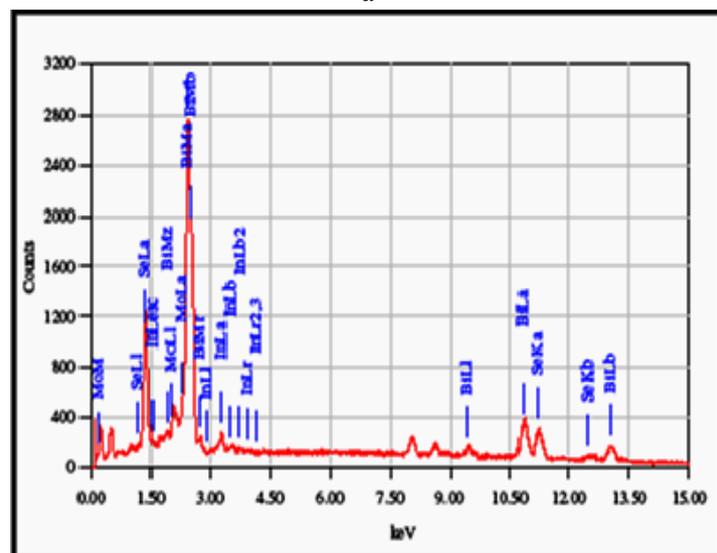
Fig. 3. 2D and 3D (A_1, A_2, A_3 and B_1, B_2, B_3) AFM images for the In doped MoBi_2Se_5 thin films samples respectively.

3.5. SEM analysis

Figure 4 shows scanning electron micrographs of In doped MoBi_2Se_5 thin films in the as-grown condition. The microstructure of the films observed by SEM shows that the films are uniform, crack free and covered all over the surface area [31]. The SEM micrograph of the samples shows spherical and elongated fibrous structure. Some regions of overgrowth were also observed. The grain size of In doped MoBi_2Se_5 thin films with $x = 0.0\text{ml}$, 0.2 ml , 0.4 ml , 0.6 ml , 0.8 ml , 1.0 ml are 999 , 994 , 989 , 984 , 977 , 970 nm respectively. All grains having average size (985.5nm) are composed of single type small densely packed crystals and appear very homogeneous.



a



3.6. EDS analysis

The stoichiometry and atomic wt% of In doped MoBi_2Se_5 thin films was found by EDS. Figure 5 shows EDS spectrum of the as deposited In doped MoBi_2Se_5 thin films. The actual and expected atomic % for various compositions of In doped MoBi_2Se_5 thin films is shown in Table 3.

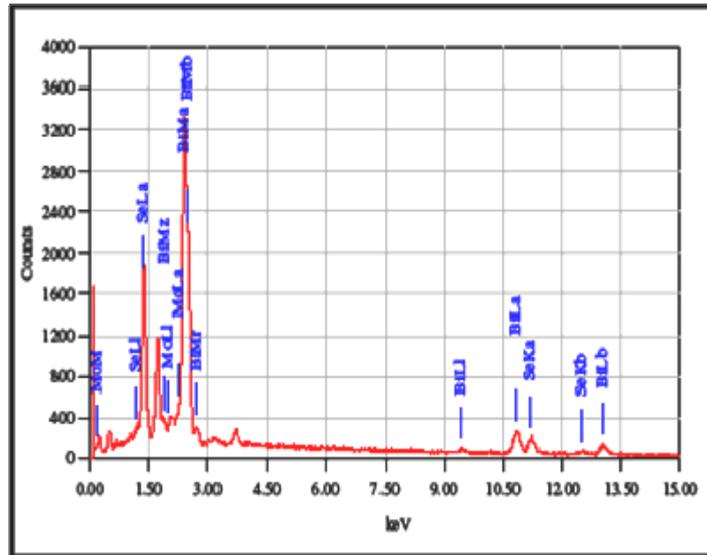


Fig. 5. EDAX for the In doped MoBi_2Se_5 thin films having different composition.

3.7. Electrical analysis

To examine the temperature dependence of the electrical conductivity in more detail, electrical conductivity measurement was made in the temperature range 300 K to 500 K under constant voltage (5 volt). The temperature dependence of electrical conductivity of the semiconducting thin films is given by [32],

$$\sigma = \sigma_0 e^{(-E_a/\kappa T)}$$

Where E_a is conductivity activation energy, κ is Boltzmann constant and σ_0 is the temperature independent part of the conductivity. The variation of $\log \sigma$ with $1/T$ in the temperature range 300 K to 500 K is shown in figure 6. The linear variation of the plot confirms the semiconducting nature of the films. The plot reveals that, the conductivity varies slowly with $1/T$ and other above 445 K, where the conductivity varies abruptly with increase in temperature. The activation energy for conduction in low temperature region is the energy required to take place between the defect level and valence band or conduction band. At sufficiently high temperature intrinsic conductivity starts and electron conduction from valence band to conduction band take place. From the slopes of linear plots, activation energy for conduction was calculated for two temperature regions. The activation energies for low temperature region and in high temperature region for In doped MoBi_2Se_5 thin films is shown in Table 4.

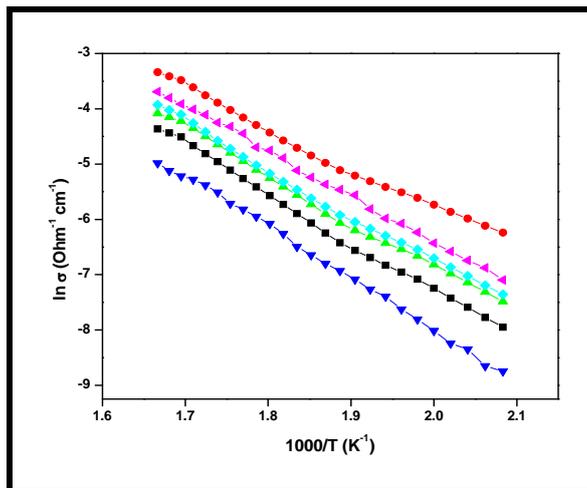


Fig. 6. $\ln \sigma$ vs. $1000/T$ plots for the In doped MoBi_2Se_5 thin films having different composition.

3.8. TEP analysis

During TEP measurement in a semiconductor, temperature gradient yields the thermo electric effect. in which phonon travel from the hot end to cold end because of electron phonon interactions. Thermo electric power (S) Vs temperature curve for In doped MoBi_2Se_5 thin films is shown in figure 7. It is clear from the figure 7 that S goes on increasing with temperature. The Seebeck coefficient of In doped MoBi_2Se_5 thin films is quite high, -ve and increases with increasing temperature. The -ve sign stems from a dominance of n-type charge carriers [33]. The temperature dependence the Seebeck coefficient of as deposited MoBi_2Se_5 and In doped MoBi_2Se_5 thin films is shown in Figure7.

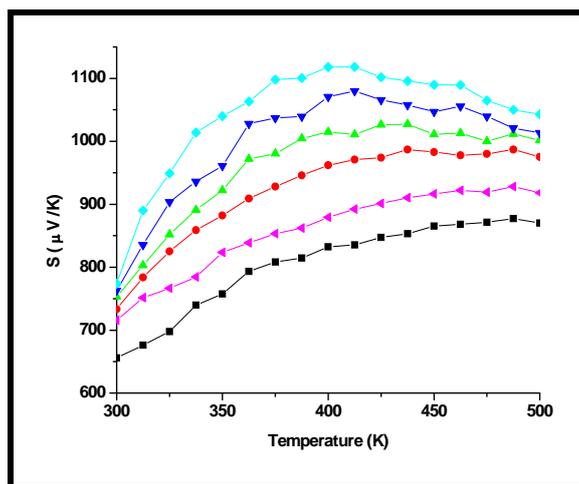


Fig. 7. Temperature dependence of the Seebeck coefficient for the In doped MoBi_2Se_5 thin films having different composition.

4. Conclusions

Arrested precipitation technique is successfully used to deposit good quality, stoichiometric, adherent and uniform deposition of MoBi₂Se₅ and In doped MoBi₂Se₅ material in thin film form. Optostructural and SEM results obtained shows material can be useful for device application such as best candidate for broadband photo convertor and as a photo electrode in solar cells. These features confirm the high quality of the chemically deposited In doped MoBi₂Se₅ thin film is applicable to the deposition of quaternary semiconductor compounds. Good quality films of thickness 1.2 to 1.5 μ m containing Mo, Bi, In and Se in an approximately 1:2:1:5 atomic ratios have been deposited successfully by arrested precipitation technique. The technique is simple and requires less monitoring. AFM study shows In doped MoBi₂Se₅ thin films is suitable for fabrication of solar cells. SEM study shows the Spherical and fibrous shaped grains uniformly grown over the surface of the substrate. X-ray diffraction patterns confirmed the proper phase formation of the material. The films are mechanically stable since no cracks are observed in the low magnification SEM image. Activation energy is different for low and high temperature regions. In doped MoBi₂Se₅ thin films exhibits an n-type semiconducting behavior with a low electrical conductivity and very high thermoelectric power, hence material is strongly applicable for the fabrication of solar cells.

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