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Effect of bismuth Doping on Structural and Electrical Properties of In_2Te_3 Thin Films

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ABSTRACT: Herein, bismuth is selected as dopant for In_2Te_3 thin films to investigate its effect on structural, electrical and thermoelectrical properties. The preferred orientation and crystallinity of Bi doped films significantly varied with different doping profile which is reflecting in X-ray diffraction patterns and scanning electron micrograph images. The thermo emf and Seebeck coefficient of prepared films is decreased with increasing Bi concentration due to change in structural properties such as crystallinity, preferred orientation and additional phases. It has been observed that there are marginal changes in electrical conductivity of Bi doped In_2Te_3 films among which 2.30 % Bi doped In_2Te_3 films are showing maximum electrical conductivity of 3.72 Ω^{-1} cm^{-1}. The maximum Seebeck coefficient is observed for 0.85 % Bi doped In_2Te_3 films. The thermoelectric power factor of 0.85 % doping of Bi is found to be enhanced by 4.8 times of undoped In_2Te_3 films.

INTRODUCTION

The materials of form $A_2^{III}B_3^{VI}$ exhibit a defect zinc blende or wurtzite structure with one- third of the cation sites vacant. Among these group of materials, Indium telluride is paying a special interest because of its attractive electrical and optical properties along with stoichiometric defects which makes them suitable for opto-electronic devices and thermoelectric applications. In_2Te_3 has large density of stoichiometry vacancies at cation sites which is ~5.5 x 10^{21} cm^{-3} due to the mismatch between lattice of indium (In^{3+}) and tellurium ions (Te^{2-}) [1–4]. Even at higher ionization fluences, In_2Te_3 has high radiation stability in electronic parameters which was experimentally examined up to 10^{18} fast neutrons per cm^2[5]. Hence, In_2Te_3 is owing the interest in various research domains due to its peculiar properties. The properties of III-VI materials have been mostly investigated in the bulk crystal form[6–8]. In spite of its good electrical and optical properties, exploitation of these materials in practical applications is limited by their poor mechanical and thermal properties. The mechanical properties of the materials can be strengthened by the thin film form which can makes them potential for device applications.

Indium telluride has good electrical conductivity (~ 0.66 Ω^{-1} m^{-1}) and less thermal conductivity (~ 1 W m^{-1} K^{-1})which makes them to exhibit good thermoelectric properties [8,9]. In addition, this material is exhibiting a direct band gap of 1.1 eV. From the scenario of both electrical and optical properties, In_2Te_3 can be used in opt-electronic applications [4,10,11]. Apart from its suitability for opt-electronic applications it has been tested for gas sensors and strain gauges [12,13].However, there are few scientific papers published on ther-

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moelectric properties of In_2Te_3 films [9,14-18]. Whereas, the study on doped In_2Te_3 films is comparitively very less [11,19,20].
From the knowledge of basic properties and literature of indium telluride, its interesting to investigate the thermoelctric propeties of doped In_2Te_3 thin films. However, in this investigation, bismuth (Bi) is selected as doping material to understand structural, elctrical and seebeck coefficient modifications caused by incorporation of Bi. Reportedly, the seebeck coefficient of undoped In_2Te_3 is 237 μ V K^{-1} with thermoelectric power factor of 4.93 μ Wm^{-1} K^{-2} at 320 K [21]. The results drawn from the experimental studies are reported in result and disscussion section from which, the thermoelctric power factor of 0.85 % Bi doped films is improved by 4.8 times of un-doped In_2Te_3 films.

METHODS/EXERIMENTAL

Closed vapour deposition technique was used to prepare both un-doped and Bi doped In_2Te_3 thin films. The residual pressure inside the chamber was maintained around 10^{-6} Torr. All films were grown at substrate temperature of 423 K on soda lime glass slidesusing resistive heating method (SMART COAT 3.0, HHV, INDIA). Chromic acid, liquid detergent and acetone were used to clean soda lime glass plates. The thickness and average growth rate of films was maintained about ~350 nm and 4.2 nm/s, respectively. In_2Te_3(ACI ALLOYS, INC, USA) pellets were used as the precursor material with 99.999% purity and dopant materials aluminium (ALFA AESAR, US) of 99.9995% purity and antimony (HIMEDIA, INDIA) of 99.9% pure pellets were used for deposition.
The structural information such as phase, orientation and lattice constants of the films were obtained using x-ray diffraction (XRD, RIGAKU MINIFLEX600) at 2θ ranging from 20 to 65°. The morphological information about the surface of prepared samples is obtained using field emission scanning electron microscope (FE-SEM, CARL ZEISS). Energy dispersive analysis of x-ray (EDX, CLASSONE SYSTEM) was used to confirm the composition of all films (error : ± 0.5 at %). The variation in electrical properties and thermo emf as a function of temperature were carried out by using a setup containing an oven and a multimeter (KEITHLEY-2002).

RESULTS AND DISCUSSION

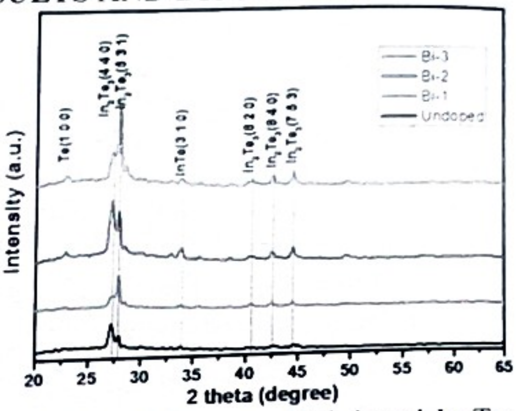

Figure 1: XRD patterns of Bi doped In_2Te_3 thin films deposited at 423 K

Figure 1 shows the XRD patterns of Bi doped In_2Te_3 films. All Bi doped In_2Te_3 films are polycrystalline in nature with multiple peaks corresponding to cubic In_2Te_3 phase along with minor contribution of hexagonal Te and tetragonal InTe phases. In Fig 4.6, (4 4 0), (5 3 1), (8 2 0), (8 4 0), (7 5 3) peaks corresponding to In_2Te_3 phase, (3 1 0) peak belongs to InTe and (1 0 0) peak corresponding to Te phases are appearing. 0.85 % and 3.04 % Bi doped films are predominantly orientated along In_2Te_3 (5 3 1) plane whereas, 2.30 % Bi doped films are dominantly oriented along (4 4 0) plane of In_2Te_3 phase. The lattice parameter of these films is calculated along In_2Te_3 (5 3 1) plane which is 18.503 Å.
FESEM micrographs of Bi-doped In_2Te_3 are given in figure 2. The surface of the In_2Te_3 films is basically granular and grain size increases with

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increasing Bi doping percentage. There are few inter-grain gaps on films surface which reduces with an increase in Bi concentration. The inter-grain gaps are more pronounced in 0.85 % Bi doped In_2Te_3 films and does not affect the films continuity due to enough thickness (~350 nm).

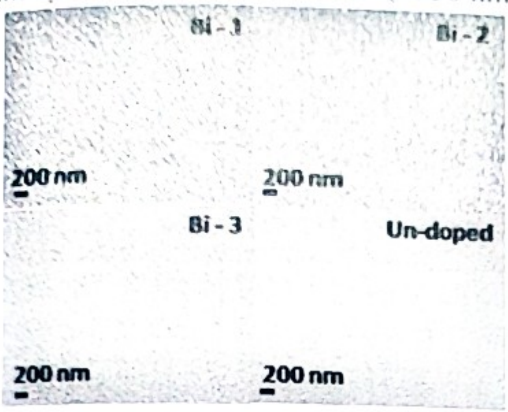

Figure 2FE-SEM micrographs of Bi doped In_2Te_3 thin films

The compositional analysis of Bi doped In_2Te_3 films revealed that Bi doping percentage in the prepared films is less than the precursor Bi percentage which might be due to the differences in vapour pressures of dopant and source material (Te>Bi>In). The elemental atomic percentage of the constituents is given in table 1. Figure 3 is an EDAX spectrum showing the presence of Bi in 0.85% Bi doped In_2Te_3 films. Similarly, all the prepared films show the presence of Bi added in bulk precursor material.

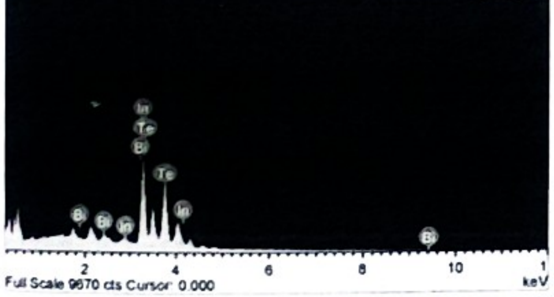

Figure 3 EDAX spectra of doped In_2Te_3 films (Bi-1).

Thermoelectric properties:

To investigate thermoelectric properties of Bi doped In_2Te_3 films, silver contacts (Ohmic) are thermally deposited on the prepared films using thermal evaporation technique. Ohmic nature of silver is confirmed from symmetric nature of current-voltage graph which means that the voltage drop across the metal-semiconductor (silver-In_2Te_3 films) interface is negligible. Figure 4 (a) represents the variation in thermo emf as a function of temperature difference.

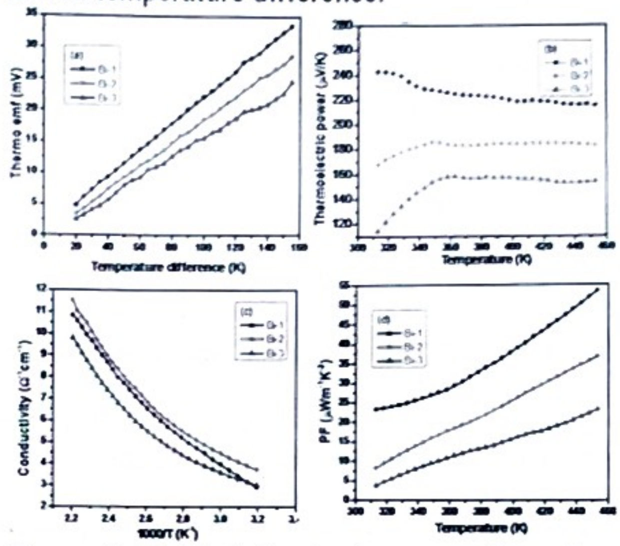

Figure 4 (a). Variation in thermo emf as a function temperature difference, **(b)**. Plot of thermoelectric power vs hot end temperature, **(c).** Electrical conductivity as function of inverse temperature and **(d).** Variation of power factor with temperature, of Bi doped In_2Te_3 films

The thermo emf of the Bi doped In_2Te_3 films is proportionally increasing with an increase in temperature but decreasing with an increase in Bi doping concentration. The slope of figure 4 (a) shows a positive nature which shows the p-type conductivity of the films. The Seebeck coefficient of these films decreases with an increase in Bi doping concentration (Figure 4.b). The Seebeck coefficient is maximum for 0.85 % Bi doped In_2Te_3 films which is 288 μ V K^{-1} at 320 K. Generally, when crystallinity of films increases then the thermo emf and Seebeck coefficient of polycrystalline thin films reduces which is due to the higher symmetry in density of states and this is the reason for poor thermoelectric behaviour of metals. However, the decrease in Seebeck coefficient of Bi doped In_2Te_3 films with an increase in doping concentration is due to amendment in crystallinity of films as shown in fig 1.

The conductivity of In_2Te_3 films is marginally affected with Bi doping which can be seen in figure 4(c). An exponential decrease in electrical conductivity with inverse temperature indicates the semiconducting behaviour of prepared films (Figure 4.c). However, 2.30 % Bi doped films are showing maximum electrical conductivity which might be due to the involvement of InTe (which have higher conductivity than In_2Te_3) phase and reduction in inter-grain gaps. The electrical conductivity of 2.30 % Bi doped films is around 3.72 Ω^{-1} cm^{-1} at 320 K.

Figure 4 (d) shows the power factor of Bi doped In_2Te_3 films as a function of temperature which is showing an increasing trend when temperature increases. As Bi doping percentage increases, the power factor of the films is found to be decreased. Since the power factor ($S^2\sigma$) depends on both electrical conductivity and Seebeck coefficient, 0.85 % Bi doped films have shown higher power factor of ~ 23.89 μW m^{-1} K^{-2} (at 320 K) which is improved by 4.8 times than that of un-doped In_2Te_3 films.

CONCLUSIONS

The doping of Bi to In_2Te_3thin films brought many changes in the structural properties of films which significantly affected the thermoelectric power and marginally influenced electrical conductivity of prepared films. In Bi doped In_2Te_3 films,2.30 % Bi dopedsamples are showing maximum electrical conductivity of 3.72 Ω^{-1} cm^{-1}. The thermoelectric power and power factor of the films were decreased with an increase in Bi percentage. The 0.85 % Bi doped In_2Te_3 films showed the maximum power factor of 23.89 μ$Wm^{-1}K^{-2}$ which was improved by 4.8 times of un-doped In_2Te_3 films.

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ABBREVIATIONS

XRD, x-ray diffraction;FE-SEM, field emission scanning electron microscopy; EDX, energy dispersive analysis of x-rays.

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Table 1 Elemental composition of Bi doped thin films

Sample names	Dopant conc. (%) in source	Film Composition (at%.)		
		Bi	In	Te
Bi-1	1%	0.85	52.49	46.66
Bi-2	3%	2.30	52.12	45.58
Bi-3	5%	3.04	52.25	44.71