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Preparation and characterization of layer-diffusion processed InBi₂Se₄ thin films for photovoltaics application

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ABSTRACT

In this research work, optoelectronic properties of Indium bismuth selenide (InBi₂Se₄) thin films are studied for their potentials for photovoltaic applications. The InBi₂Se₄ films are prepared via a thermal co-evaporation technique on glass substrate using Bi₂S₃ powders and indium granules. The as-deposited films are then annealed at different temperatures to convert into InBi₂Se₄ thin films. Results show that the obtained InBi₂Se₄ films possess excellent optoelectronic properties as an optimum bandgap of 1.2 eV was obtained for the film annealed at 350°C. Based on characterisation results of current and voltage realiationships, both as-deposited and annealed InBi₂Se₄ thin films show a linear relationship between current and annealing temperature. It was also noted that with increasing grain-size of the film, the current is also increased at a fixed applied voltage.

Keywords: InBi₂Se₄; Thin films; Photovoltaics; Annealing; Diffusion;

Introduction

Bi_2Se_3 has the potential of commercial production in a large area with low fabrication costs [1]. It is a topological insulator with a high surface conductivity and serves as an insulator in its bulk form. Bi_2Se_3 is commonly used in hole-transporting, and its crystallized phases can be easily processed using a solution method at room temperature [2, 3]. Bi_2Se_3 has been used extensively in photoelectrochemical (PEC) cells, solar selective decorative coatings, Hall magnetometers, photodiode arrays, and electrodes in solar cells [4, 5]. However, the high vapor pressure of selenium during the formation of the Bi_2Se_3 compound makes it very sensitive to substrate temperature. The Se vacancies in Bi_2Se_3 causes it having an n-type conductivity, and a dual conductivity is expected for Bi_2Se_3 with the controlled Se vapor pressure [6, 7].

Indium selenide is a binary compound with ~ 2 eV bandgap and an n-type conductivity. It is widely used in photovoltaic device fabrication as a window/absorbing layer, and exists in different phases such as InSe , In_2Se_3 , In_4Se_3 , In_6Se_3 [8]. It is also a layered semiconductor and can be easily deposited using electrodeposition technique, molecular beam epitaxy, flash evaporation, and chemical vapor deposition [9]. A moderate annealing temperature around 100°C is capable of achieving crystallization of InSe thin film deposited by co-thermal evaporation techniques. The conductivity of InSe is controllable with the thickness of the material though a grain boundary scattering mechanism. However, it is noted that the indium rich film has large defects densities, as a result, the carrier recombination process is increased and thus the device efficiency is reduced [10, 11]. It has many potential technological applications such as "phase-change random access memory (PRAM)" devices, solar cells, photosensors, buffer layer material, wide energy range photo-detectors, and lithium-ion batteries [12, 13]. Moreover, InSe has dual conductivity and dual bandgap (direct and indirect) depending upon growth conditions and intercalation circumstances and doping [14].

Although Bi_2Se_3 and InSe have shown potential applications in technology especially in photovoltaics, both of them need further improvement for their high-quality applications in the state of the art commercial technologies. Due to the current interest in chalcogenide materials and their potential in optoelectronic and photovoltaic properties, we will focus on our work to achieve a high performance and single ternary compound of InBi_2Se_4 thin films [15]. In this paper, we report the properties of chalcogenide-based InBi_2Se_4 materials for solar cell

applications by depositing the above two layers via thermal evaporation techniques, the obtained InBi_2Se_4 thin films are characterized to be a good absorbing layer material for thin-film solar cell technology.

Experiment

Indium bismuth selenide (IBS) thin films were fabricated using co-evaporation techniques using a thermal coater (Edward 306) from Bi_2Se_3 99.99% pure powder heated at 600°C and indium granules heated at 155°C . The distance between the source and substrate was adjusted to be ~ 8 cm while the pressure of the chamber was maintained at $\sim 2 \times 10^{-5}$ mbar. For the deposition process, soda-lime glass was used as a substrate which was washed carefully with deionized water plus acetone in an ultrasonic bath. The annealing of the obtained thin films was performed at 150°C , 250°C , and 350°C for 1 hour in a vacuum furnace. The structural analysis was done using an X-ray diffractometer (X-ray D-8 Discover XRD) with a $\text{CuK}\alpha$ radiation (with an X-ray wavelength of 1.54 Å) as an energy source. A 4-probe Keithley Source Meter (Keithley 2400) was used for the current and voltage (I-V) characterization. Optical properties of the films were explored using a UV-VIS spectrometer. To obtain compositions and chemical bonding information of the films, an X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra) was used, with $\text{Al K}\alpha$ radiation (1486.6 eV) source.

Results and Discussion

XRD pattern of the as-deposited and annealed indium bismuth selenide thin films are shown in Figure 1. The as-deposited films are nearly amorphous because only few crystalline peaks are present in the pattern. The only focal peak in the as-deposited film is at (-312) while the other peaks are at (711) are minor ones. However, with the increasing annealing temperatures, the films show their polycrystalline nature. The film annealed at 150°C show the best quality of XRD peaks. At an annealing temperature of 250°C , a few strong diffraction peaks start appearing which indicates that the crystallization with annealing is enhanced, e.g., (-514) and (-111) peaks. For the sample annealed at 350°C , more strong diffraction peaks for InBi_2Se_4 were observed as can be seen from Figure 1.

The crystalline size D of the thin film annealed at 350°C (peak position $\theta=27.099^\circ$) and peak broadening (β) can be calculated by the method of Williamson-Hall analysis [16, 17].

$$\beta = \frac{K\lambda}{D\cos(\theta)} + \epsilon \tan(\theta)$$

where K is used for Scherrer's constant (0.9), λ is a symbol used for the wavelength (Cu monochromatic $K\alpha$ lines, $\lambda= 1.54060 \text{ \AA}$) and ϵ represents the microstrain of the crystal while D stands for the crystallite size. When $\beta\cos(\theta)$ is plotted as a function of $4\sin(\theta)$, a straight line is attained (figure 2). The slope of this line is used to determine the micro-strain of the crystallites, while the average crystallite size is determined from the intercept [17]. The relation, $\delta = \frac{1}{D^2}$ is used to determine the line defects corresponding to the density of the dislocation. The surface density of the crystallite (N) can be measured by using the equation of $N = \frac{t}{D^3}$, where t represents the film thickness. The average thickness of the film was measured around 750 nm using a quartz crystal monitor during the deposition. The above mentioned results for the material structural parameters are tabulated in Table 1.

Table 1: Structural parameters of the annealed sample of the InBi_2Se_4 thin film at 350°C.

No	Parameters	Value
1	Crystallite size (D)	116.18 \AA
2	Strain (ϵ)	9.2×10^{-3}
3	Dislocation density (δ)	$7.43 \times 10^{15} \text{ nm}^{-2}$
4	Number of crystallite per unit area (N)	$11.996 \times 10^5 \text{ nm}^{-2}$

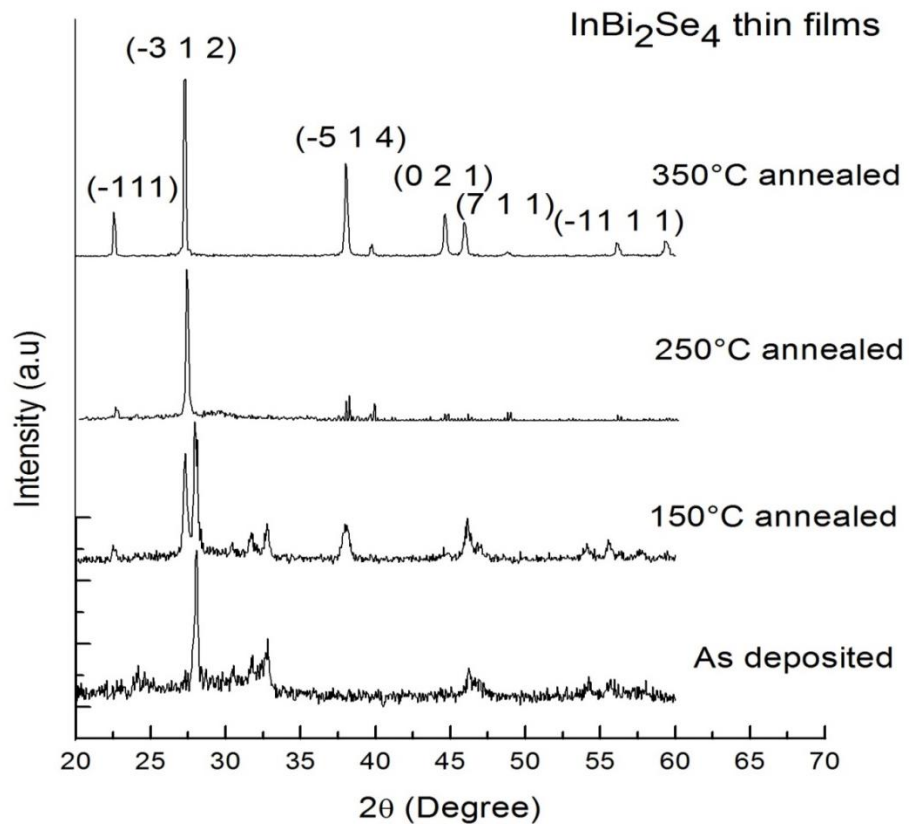


Figure 1: XRD analysis for Indium bismuth selenide

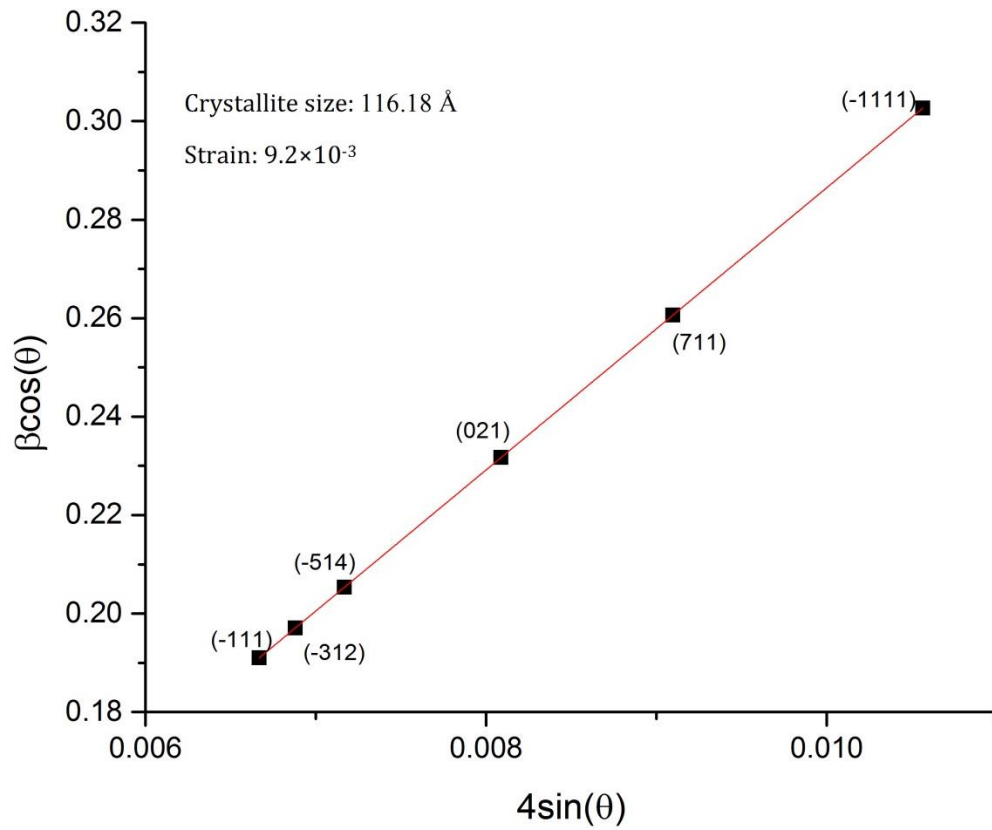


Figure 2: Williamson-Hall analysis of IBS films. The crystallites size is approximately 11.6 nm.

Table 2: Crystallographic data for InBi_2Se_4

Space group	Monoclinic
a (Å)	20.83200
b (Å)	4.1140
c (Å)	11.95800
Volume	903.61 \AA^3
Crystal size	116.18 Å

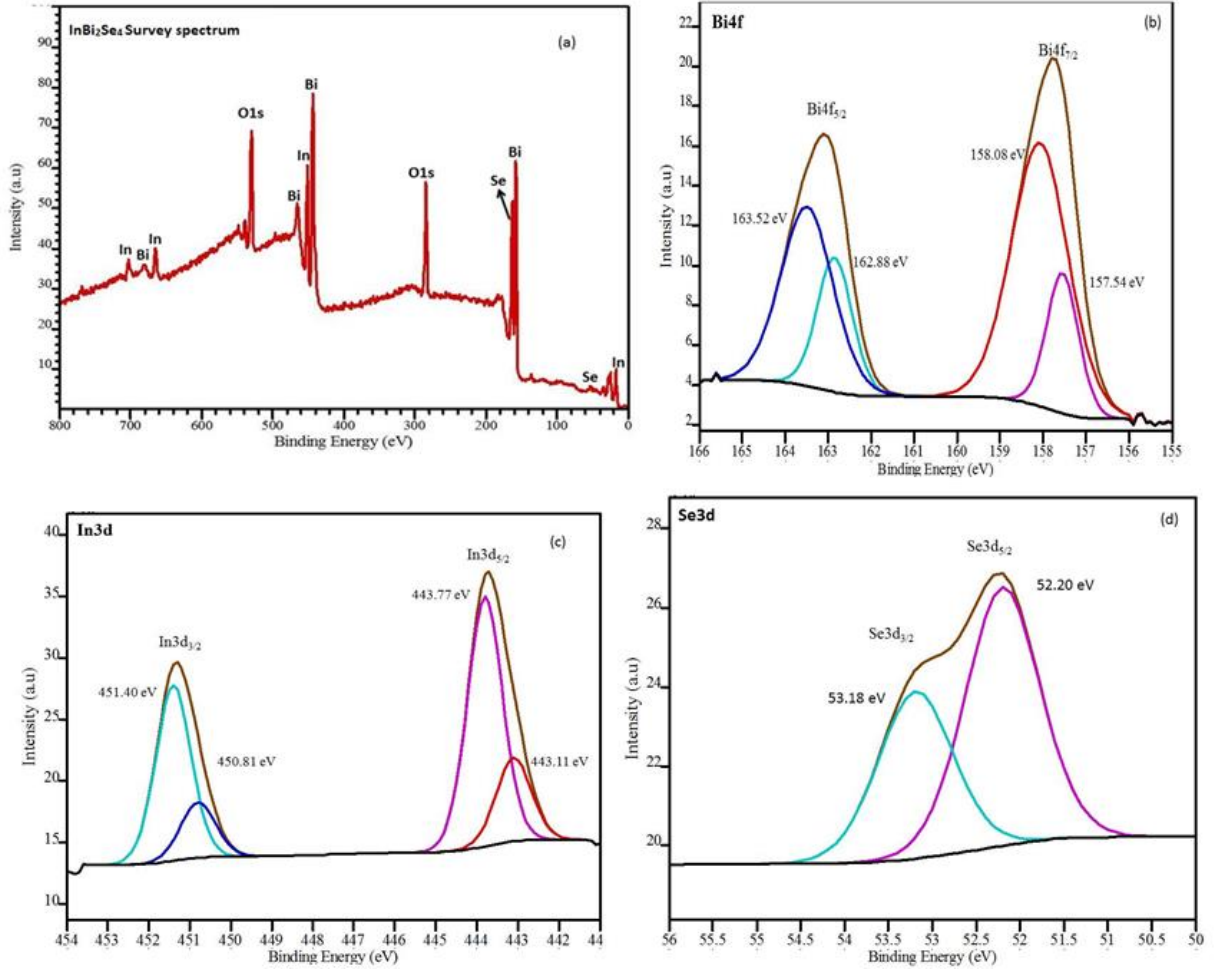


Figure 3 (a-d): The high-resolution XPS spectra of the identified three main elements; (a) survey spectrum; (b) Bi 4f; (c) In 3d; and (d) Se 3d

XPS analysis was performed for the determination of chemical bonding of the synthesized InBi₂Se₄ films. Figure 3(a) shows a typical survey spectrum of the InBi₂Se₄ annealed thin films at 350°C in which Bi, In and Se elements are found. The bismuth high resolution spectrum at the core level of a 4f doublet state is shown in Figure 3(b). The peaks corresponding to the 4f doublet state were found at 163.1 and 157.76 eV which are consistent with the reported XPS data of Bi₂Se₃. The above mentioned binding energies with a peak separation energy value of 5.34 eV correspond to doublet state Bi-4f_{7/2} and Bi-4f_{5/2}. The peaks are found at 163.52 eV and 162.88 eV for Bi 4f_{5/2}, and those for Bi 4f_{7/2} are at 158.08 eV and 157.54 eV, respectively. Due to surface adsorption, the component peaks associated with Bi-O, with a peak separation of

5.42 eV, are found to be positioned at 163.52 eV and 158.08 eV, respectively [18, 19]. Oxidation is found as a common problem in these Bi thin chalcogenide films [1]. Figure 3(c) shows a high-resolution XPS spectrum of the In, and the major peaks are observed at 443.7 eV and 451.3 eV with a difference of energy 7.6 eV between the peaks. These peaks are in the binding energy range of In 3d_{3/2} and In 3d_{5/2} for In³⁺, respectively, suggesting In³⁺ nature of the synthesized InBi₂Se₄ annealed thin films after annealed at 350°C. The peaks found at the positions of 52.2 eV and 53.18 eV correspond to Se 3d_{3/2} and Se 3d_{5/2}, respectively, with a peak separation of 0.98 eV. These XPS data are comparable with the available data reported in the literature [20]. The binding energy values corresponding to the Se 3d are within the energy range (52-53 eV), which was estimated for the selenide phase in Figure 3(d). The proportion ratio of the peaks obtained for In (3p), Bi (4f), and Se (3d) is found 1:2:4, indicating the formation of InBi₂Se₄ thin films. These obtained XPS results are in a good agreement with XRD results of the thin film annealed at a temperature of 350 °C.

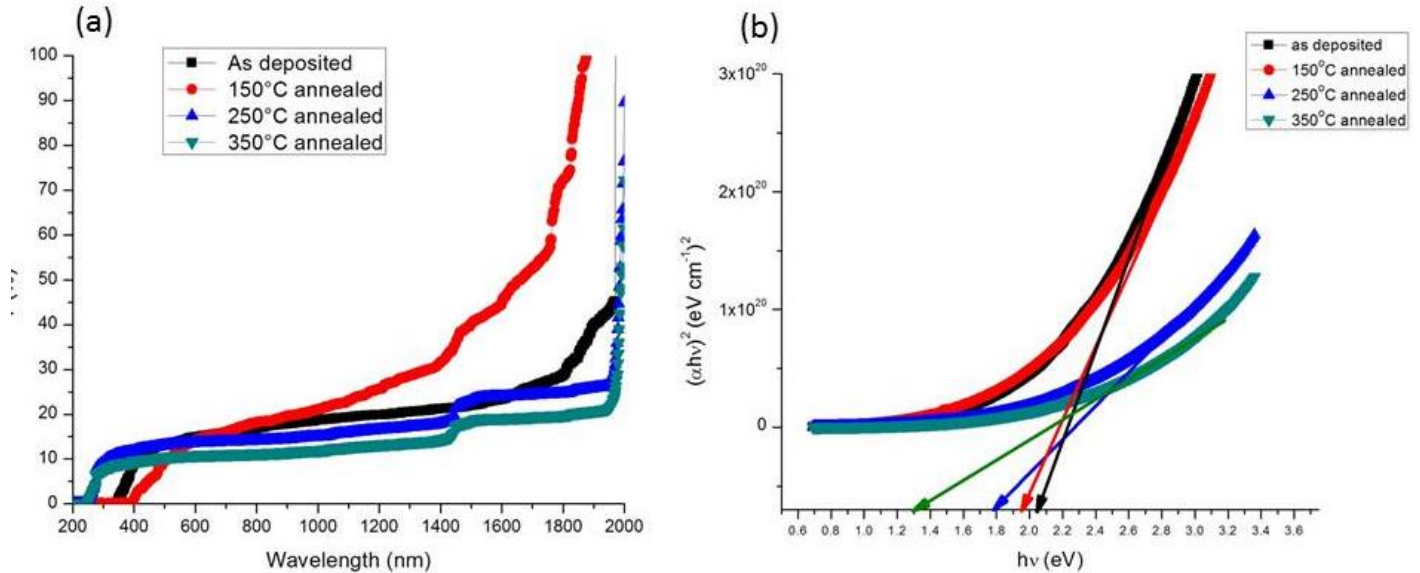


Figure 4: (a) Transmittance spectra InBi₂Se₄ (b) Band gap calculation.

Figure 4(a) shows the spectroscopic results obtained via UV-Vis spectroscopy which shows the transmittance spectra of the annealed and as-deposited thin films of InBi₂Se₄. InBi was reported as semi-metallic material in nature with an optical bandgap of 1.5 eV at 300°C [20]. However, the addition of selenium has transferred its semi-metallic nature to a semiconductor one with a

high degree absorption. The transmittance spectra shown in figure 4(a) for the annealed and as-deposited samples show clearly the good transmittance region above visible and IR wavelength range. It shows that the transmittance becomes decreased with increase of the annealing temperature. A maximum decrease, in the transmittance spectra, was noted at the 350°C annealed sample.

To calculate the bandgap [21], the absorption coefficient (α) of the annealed and as-deposited thin films is determined by using the following relation:

$$\alpha = \frac{1}{d} \ln \left(\frac{I_0}{I} \right) \quad 1$$

$$\alpha h\nu = A(h\nu - E_g)^n \quad 2$$

where d denotes thin film thickness, I_0 and I are used for the intensities of the incident and transmitted light while in equation (2), $h\nu$ represents the photon energy, A and n are transition constant and transition coefficient (where $n=1/2$ and $n=2$ for the direct and indirect allowed bandgap transition). Figure 4(b) shows the obtained plot between $(\alpha h\nu)^2$ vs. $h\nu$ which is used for estimating the bandgap energy. To do so, the linear part of the plot is extrapolated to zero-abscissa which intercepts the x-axis [12, 22]. The values of the bandgap energy for the samples annealed at 150°C, 250°C, and 350°C are 1.95 eV, 1.78 eV, and 1.3 eV, respectively, whereas the as-deposited thin film sample has a bandgap value of 2.05 eV. The decrease in the bandgap energy with annealing temperature is due to an increase in the grain size and the improved crystallinity of the annealed films.

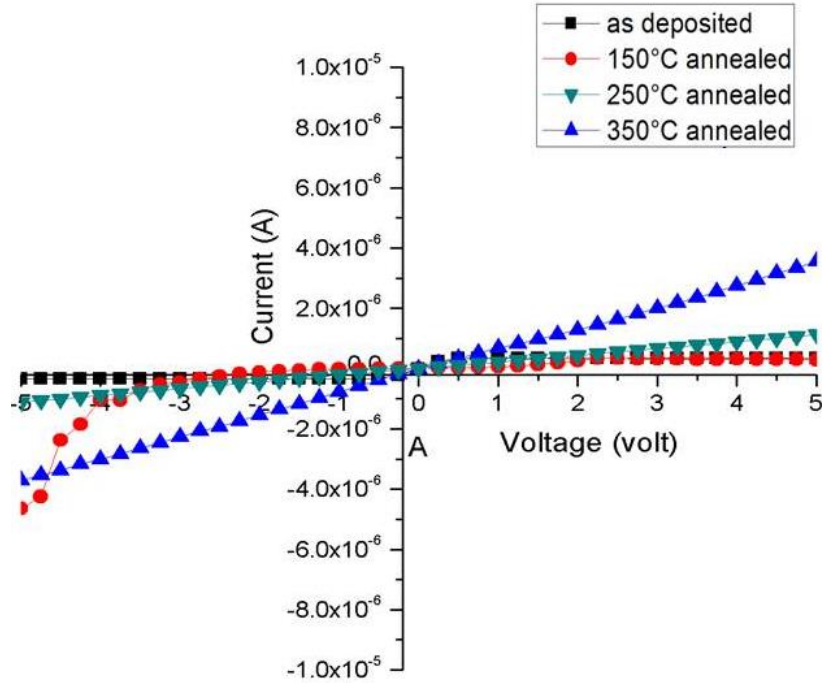


Figure 5: The current-voltage characteristics InBi₂Se₄ thin films.

The current-voltage graphs for the annealed and as-deposited samples of the thin films of InBi₂Se₄ are illustrated in Figure 5. The rectilinear correlations between current and annealing temperatures can be obtained for all the samples with an incremental rise of current with respect to the applied voltage. The increase in the current with respect to the applied voltage is an outcome of the increased crystallinity and crystallite size with the increase of annealing temperature. With the rising annealing temperature, the density of the grain boundaries is decreased and the carrier concentrations are increased, therefore, the electrical conductivity of the annealed thin films is also increased.

Conclusions

InBi₂Se₄ thin films were grown on glass substrates using thermal evaporation techniques. Structural and optoelectronic properties of the as-deposited thin films and those annealed at 150°C, 250°C and 350°C were studied. The films annealed at 350°C were found to have an orthorhombic polycrystalline crystal structure with highly oriented texture. The nature of the chemical bonding of the synthesized InBi₂Se₄ thin films along with their binding energies was

studied using the XPS. The deconvolution plots for the Bi revealed the high oxidation levels due to surface contamination and In^{3+} nature of the synthesized InBi_2Se_4 films. The optical study was carried out in the spectral range 200–2000 nm for thin films. The energy gap was found to be decreased with increasing annealing temperature, indicating that the optical absorption in these films follow the rule of direct transitions. The bandgap of 1.3 eV obtained for the 350°C annealed thin film indicates its excellent photovoltaic property. The good electrical conductivity of the films i.e. a current of 4 μA at a voltage of 5V for the annealed thin film annealed at 350°C also shows that the obtained InBi_2Se_4 film is a good photovoltaic material.

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