

Studies on physical properties of $\text{Bi}_{40-x}\text{In}_x\text{Se}_{60}$ thin films

Saleh S.A.^{*1-2} Asma Hendi³ and I. A. Abdel-Latif¹

¹Physics Department, College of Science & Arts, Najran University, P. O. 1988 Najran, Kingdom of Saudi Arabia

²Physics Department, Faculty of Science, Sohag University, Sohag 82524, Egypt

³Physics Department, Sciences Faculty for Girls, King Abdulaziz University, P. O. 80200, P. Code 21589, Jeddah Kingdom of Saudi Arabia

*saleh2010_ahmed@yahoo.com ihab_abdellatif@yahoo.co.uk

Abstract: A new series of $\text{Bi}_{40-x}\text{In}_x\text{Se}_{60}$ ($1.6 \leq x \leq 13.2$ at. %) transparent semiconducting thin films was deposited by the e-beam technique. X-ray diffraction (XRD), Field emission scanning electron microscope (FESEM), Raman spectra, electrical conductivity and UV-vis-near-IR diffuse reflectance spectra (UV-vis) were used to characterize these films. The glassy nature and the macroscopic homogeneity of the glasses were confirmed by X-ray diffractometry and Field emission scanning electron microscopy (FESEM). The structure was deduced from Raman spectra measured for all indium content in Bi-In-Se matrix. The variation of dc conductivity with temperature in the studied temperature range shows negative exponential behavior (semiconducting behavior). The optical absorption edge was described using the 'direct transition' model. The optical band gap of the film was determined.

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1. Introduction

Thin chalcogenide films have recently gained considerable attention due to their interesting physical (optical and electrical) properties and technological applications. All possible applications emerge from their optical and electrical properties which are closely related to their structure and composition. One of the recent applications of these materials is electrical nonvolatile memory device known as chalcogenide random access memory (C-RAM) [1], which is also named phase-change memory (PCM) [2], phase-change random access memory (PCRAM [3] or PRAM [4]) or ovonic unified memory (OUM) [5]. This technology is based on reversible phase transition between crystalline (low resistivity, semi-metal) and amorphous (high resistivity, semiconductor) states. The phase change is realized via optical pulses or electrical pulses, whereas detection consists in difference of optical reflectivity or electric resistance of both phases [6].

Active materials in phase change based memories are currently chalcogenide materials [7]. The benefit of these materials consists in possibility of easily feasible reversible phase change. In addition, the rates of phase changes are high and stability of both phases in ambient conditions are relatively good. The most favorable systems are currently based on Sb-Se binary system with addition of some other elements such as Ge, In, Ag, etc. Bi-Se is also a promising material for the same applications. Although, the physical properties of Bi_2Se_3 thin film have been studied [8-12], there are

no data reporting optical band gap, electrical resistivity and temperature dependence of dc conductivity of the amorphous and crystalline states of Bi-In-Se thin films. For technological application in optical and electrical memory devices, the knowledge of these properties becomes a fundamental issue.

In the present work, we have reported and discuss the composition dependence of the structural, electrical and optical properties of $\text{Bi}_{40-x}\text{In}_x\text{Se}_{60}$ ($x = 1.6, 4.4, 10$ and 13.2 at.%) thin films deposited at room temperature on glass substrates using the electron beam technique.

2. Experimental

Production of the concerned materials was carried out through two processes. The first was the preparation of different alloys using the usual melt quenching technique by sealing, under a vacuum of 10^{-5} Torr, the appropriate atomic percentages of high purity Bi, In and Se ($\sim 4\text{N}$) in cylindrical quartz ampoules. The sealed ampoules were then placed in an electric furnace and heated to a temperature of 800°C for two days. The ampoules at this temperature were frequently shaken in order to homogenize the melt. After completing the melting process, the ampoules were quenched to 0°C in an ice-water mixture. The second process implies the deposition of amorphous Bi-In-Se films by an electron beam evaporation of the bulk alloys in a vacuum of 2×10^{-5} Torr. The deposition was carried out on ultrasonically clean glass substrate kept at 300 K by using Edward's high vacuum coating unit

model E306A. The deposition parameters were kept constant for all investigated films. The film thickness was measured by a digital thickness monitor (TM200 Maxtek) and was found to be approximately 200 nm. The structure of the deposited films was identified using X-ray diffractometer PANalytical (X' pert Pro MPR) with Cu K_{α} radiation. Surface morphological studies were carried out by means of scanning electron microscope SEM, Joel JSM 7600F equipped with EDX analyzer. Raman spectra of the films were recorded at room temperature using Perkin Elmer (Raman station 400) Raman spectrometer within a wave number range $3000-100\text{ cm}^{-1}$ at λ -exciting wavelength 514.5 nm. For DC conductivity measurements, the samples were mounted in a specially designed sample holder under a vacuum of about 10^{-3} torr. A DC voltage (1.1V) was applied across the sample and the resulted current was measured by a digital picoammeter (DPM-111 Scientific Equipments, Roorkee). The temperature was measured by a calibrated copper-constantan thermocouple mounted near the sample. The transmittance and reflectance were measured using a double beam dispersive spectrophotometer Jasco V-570 in the spectral range 200 - 2500 nm.

3. Results and Discussion

3.1. Structural studies

The X-ray diffractograms depicted in Fig.1 show a presence of only broad features with absence of any sharp peak. These broad features indicate that the films are amorphous in nature. The compositional analysis of the thin films indicates that the elemental chemical composition of Bi: In: Se was found to be 38.4: 1.6: 60, 35.6: 4.4: 60, 30: 10: 60 and 26.8: 13.2: 60, respectively. The estimated average deviation does not exceed 2% in atomic fraction from the desired stoichiometry of each element. The scanning electron micrograph of $\text{Bi}_{38.4}\text{In}_{1.6}\text{Se}_{60}$ thin film (Fig. 2-a) shows smooth and uniform surface without cracks as well as adherent to the glass substrate. The SEM image (Fig. 2-b) suggests the presence of some particles in nano size embedded in an amorphous matrix which are in agreement with the XRD results. The appearance of this nanophase in the as-deposited films may be due to increasing the In content in the composition, which increases the crystallization ability. This result matches well with some previously reported data [13-14].

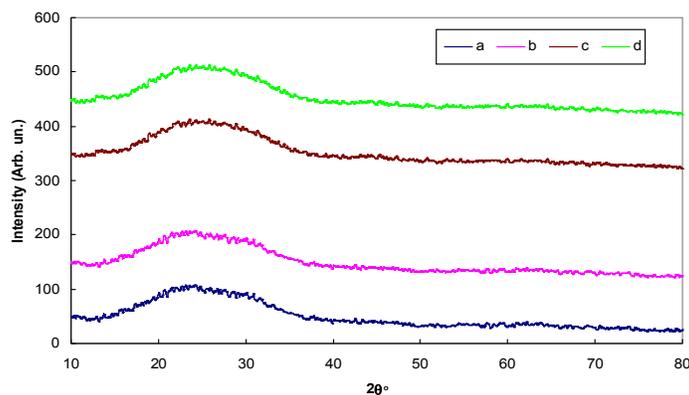


Fig. (1) X-ray diffractogram of a) $\text{Bi}_{38.4}\text{In}_{1.6}\text{Se}_{60}$ b) $\text{Bi}_{35.6}\text{In}_{4.4}\text{Se}_{60}$ c) $\text{Bi}_{30}\text{In}_{10}\text{Se}_{60}$ and d) $\text{Bi}_{26.8}\text{In}_{13.2}\text{Se}_{60}$ thin films.

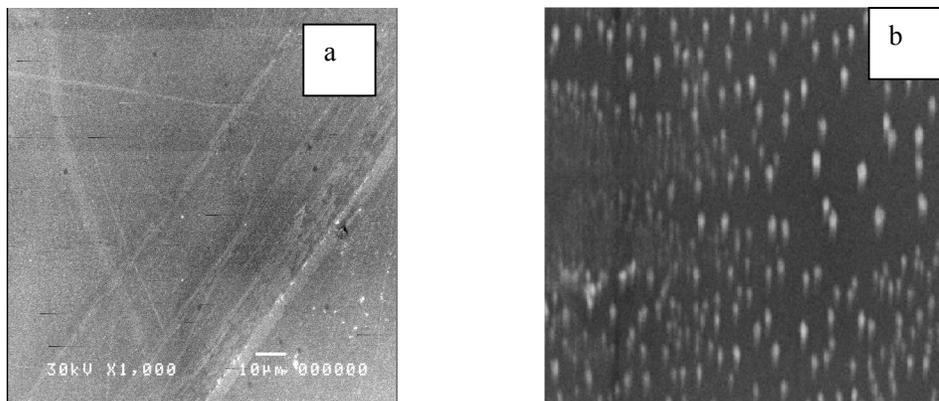


Fig. (2) SEM photos of $\text{Bi}_{38.4}\text{In}_{1.6}\text{Se}_{60}$ a) $x = 1000$ and b) $x = 13000$

It is well known that the vibrational spectroscopy is extremely sensitive to the electronic structural changes. Raman spectra of all films are studied in order to obtain the molecular structure. The vibrational bands reported in the literature concerning the crystallinity of some similar compositions have been taken as references for discussing of the spectra [15]. Raman spectra of our $\text{Bi}_{40-x}\text{In}_x\text{Se}_{60}$ thin films are shown in Fig. (3). No significant change in the shape and position of the characteristic vibration bands with the increase in indium content could be observed. The broad bands located around 170, 148 and 122 cm^{-1} . The 170 band is attributed to Bi_2Se_3 and In_2Se_3 pyramidal units. The Raman spectra indicates that the presence vibrational modes is due to Bi(In)Se_3 structural unit. The vibration spectra must correspond primarily to

vibrational modes involving Bi-Se bonds as Se-Se bonds would be highly unexpected in these Se-poor materials and stretching modes of Bi-Bi homopolar bonds. The basic structural units of ternary (Bi-In-Se) system is expected to be BiSe_3 pyramids with three-fold coordinated Bi atom at the apex and InSe_3 pyramids with three-fold coordinated In atom at the apex which are weakly coupled through two atomic-Se-Se bridging groups [16]. A change in the peak intensity and the peak position may be attributed to an increase in structural randomness [17]. Also, it is derived that the changes occur non-monotonically with increasing In content. Fig. (3) reveals that most of the peaks have shifted to either higher or lower values with increasing the In content. This may affect the population of charge defect centers and hence the electrical conductivity.

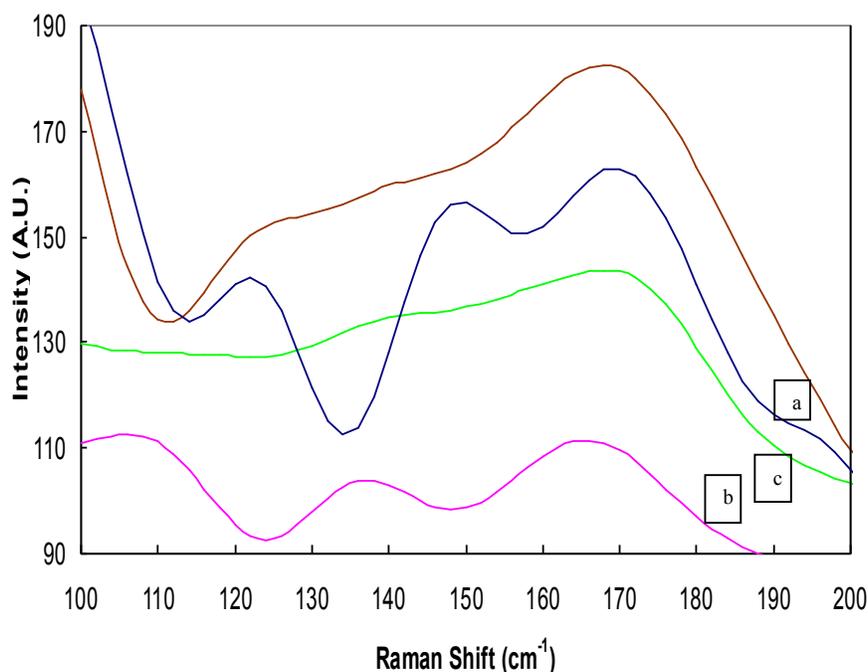


Fig. (3) Raman spectra of four films a) $\text{Bi}_{38.4}\text{In}_{1.6}\text{Se}_{60}$ b) $\text{Bi}_{35.6}\text{In}_{4.4}\text{Se}_{60}$ c) $\text{Bi}_{30}\text{In}_{10}\text{Se}_{60}$ and d) $\text{Bi}_{26.8}\text{In}_{13.2}\text{Se}_{60}$

3.2. Electrical studies

In order to obtain the general behavior of electrical conductivity and gather information about current transport mechanisms, the conductivity data has been analyzed to distinguish between the possible mechanisms in thin films namely; thermionic emission, thermally assisted tunneling and variable range hopping. For Bi-In-Se films (200 nm thick each) of various In contents, temperature dependence of dark electrical conductivity was studied during heating from ambient temperature to

200°C at a fixed rate of 10 °C/min. It was observed that, for each film, the conductivity increases linearly with increasing the temperature up to a certain value (T_c) at which a sudden increase occurs indicating the crystallization of the amorphous films [18]. Above T_c , the conductivity increases at a much lower rate than in the amorphous materials. It is worth noting that, this increase is more pronounced in samples with higher In concentration. Hence, one can observe that the vs. T plots are characterized with two distinct regions corresponding to low and high temperature

ranges suggesting a transition between two different mechanisms. In high temperature region the abrupt increase in σ means that the conduction is thermally activated and can be described by the following Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E_\sigma/K_B T)$$

where the pre-exponential factor σ_0 depends on the composition of the films [18], K_B is the Boltzmann's constant, T is the absolute temperature and E_σ is the corresponding activation energy, which is a function of the electronic energy levels of chemically interacting atoms in the amorphous materials and hence of the emerging band gap. The linear dependence of $\ln \sigma$ with the reciprocal temperature, observed in Fig.4, confirms the thermally activated conduction mechanism [19, 20]. Previous publications have reported a similar behavior in the conductivity of other amorphous chalcogenide materials [21, 22]. The activation energy values E_σ of the materials were calculated and tabulated in Table (1). In the low temperature region, $\sigma(T)$ exhibit relatively less thermal activation suggesting that the conduction is due to the Mott's VRH in localized

states near the Fermi level. This VRH mechanism is characterized by Mott's expression [23] of the form:

$$\sigma = \sigma_1 T^{-0.5} \exp(-AT^{-0.25})$$

$$\text{with } A^4 = T_o = \frac{16 \alpha_o^3}{K_B N(E_f)}$$

Here T_o is the degree of disorder, σ_1 is the pre-exponential factor, $N(E_f)$ is the density of localized states participating in hopping conduction, α_o describes the spatial extent of the localization wave function and is assumed to be 0.124 \AA^{-1} [24] and K_B is Boltzmann's constant. Values of σ_1 , T_o , $N(E_f)$ as well as the room temperature values of hopping distance R and hopping energy W (in Mott's theory

$$R = \left(\frac{9}{(8 \pi \alpha_o K_B T N(E_f))} \right)^{0.25} \text{ and}$$

$$W = \frac{3}{4 \pi R N(E_f)^3}$$

listed in Table 1.

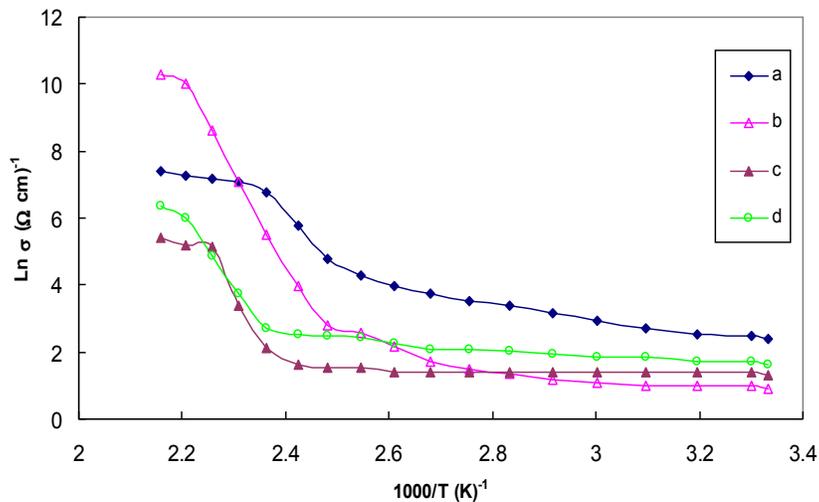


Fig. 4. Plot of $\ln \sigma$ vs. $(1000/T)$ for all films. $\ln \sigma$ set variation of E_σ with \ln content in four films. Solid line is drawn through data points to guide the eye.

Table 1) Parameters of $\text{Bi}_{40-x}\text{In}_x\text{Se}_{60}$ ($1.6 \leq x \leq 13.2$ at.%) thin films.

In at.%	E (eV)	1	A (k) ^{0.25}	T _o	N(E _f)10 ¹⁸ (eV ⁻¹ cm ⁻³)
1.6	1.038768	21	109	141158161	2.64
4.4	1.804992	15.7	94	78074896	4.76
10	1.716048	-----	-----	-----	-----
13.2	1.537344	5.74	39	2313441	185.77

3.3. Optical studies

Study of the optical properties of $\text{Bi}_{40-x}\text{In}_x\text{Se}_{60}$ ($1.6 \leq x \leq 13.2$ at. %) films, particularly the absorption edge gives valuable information on the electronic structure of the material. The absorption coefficient α was computed according to the following expression [25-27]: $\alpha = \text{OD}/d$ where OD is the optical density measured at a given layer thickness (d). The obtained values of α as a function of wavelength (λ) for $\text{Bi}_{40-x}\text{In}_x\text{Se}_{60}$ thin films are illustrated in Fig.5. The optical energy gap, E_g^{opt} , for Bi-In-Se films can be calculated from the well-known quadratic equation [28-30], which is often called Tauc's law $\alpha h\nu = \beta (h\nu - E_g^{\text{opt}})^r$ where $h\nu$ is the incident photon energy, β is a constant that depends on the electronic transition probability and the exponent r is a parameter which depends on the type of electronic transition responsible for the absorption. Values of $r = 2$ and $r = 0.5$ correspond, respectively, to allowed indirect and allowed direct optical transitions. Here, $r = 0.5$ offers the best fit for the optical absorption data of the investigated films. The optical absorption coefficient is of the order of 10^6 m^{-1} supporting the allowed direct band transition of the material [9,10,31]. The optical band gap E_g^{opt} is determined near the absorption edge by extrapolating the straight portion

of the plot of energy axis. The E_g^{opt} of the as-deposited film decreases with increasing In content as shown inset. This change may be understood on the basis of the change in average bond energy as a function of composition. Since optical band gap is a bond sensitive property [32], a decrease in the average bond energy results in a decrease in E_g^{opt} . This may be due to that, the addition of In produces localized states near the conduction band edge, so that the electrical transport is due to the hopping of electrons after being excited into localized states at the conduction band edge. These results are in good agreement with previously reported results [33-34]. Also, the observed change of energy gap for all films can be explained using the density of the states model in amorphous solids proposed by Mott and Davis [21]. Accordingly, the width of the localized states near the mobility edges depends on the degree of disorder and defects present in the amorphous structure. In particular, it is known that the unsaturated bonds are responsible for the formation of some defects in amorphous solids. Such defects produce localized states in the band structure. The presence of a high concentration of localized states is responsible for relatively low values of the optical gap in the case of the as-deposited amorphous films [35].

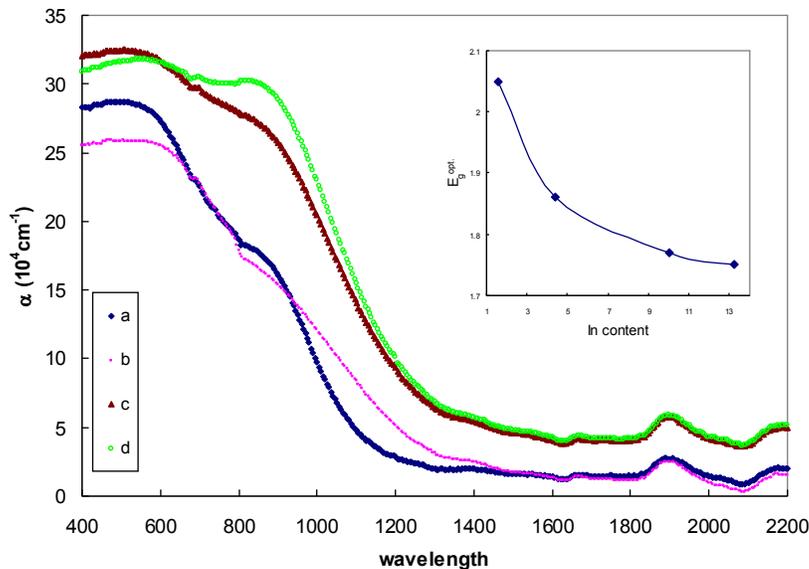


Fig. (5) Plot of absorption coefficient with wavelength for as-prepared films. In set Variation of E_g^{opt} with In content in four films. Solid line is drawn through data points to guide the eye.

Conclusion

$\text{Bi}_{40-x}\text{In}_x\text{Se}_{60}$ ($1.6 < x < 13.2$) thin films prepared by electron beam evaporation have been studied by XRD, SEM and Raman analysis. The structure of all deposited thin films is amorphous. All deposited thin films are chemically homogeneous with smooth

surface. The temperature dependence of the dc electrical conductivity through the temperature range $25 - 200^\circ\text{C}$ suggests that there are two types of conduction mechanisms that contribute to the conductivity. The calculated value of activation energy indicates that the as-deposited films behave as

semiconductor material. The optical transitions in all films have been found to be allowed and direct.

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Corresponding author

Saleh S.A

Physics Department, College of Science & Arts, Najran University, P. O. 1988 Najran, Kingdom of Saudi Arabia

Physics Department, Faculty of Science, Sohag University, Sohag 82524, Egypt
saleh2010_ahmed@yahoo.com

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