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Synthesis and characterization of bismuth selenide thin films by thermal evaporation technique

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In recent years, bismuth selenide has attracted a good deal of attention due to its unique properties. Bismuth selenide is a topological insulator which has surface conductivity that makes it an attractive compound for practical applications. Employing the solid state reaction, bulk bismuth selenide compounds in four different stoichiometric ratios of Bi/Se have been prepared at 850 °C in a muffle furnace. The synthesized bismuth selenide compounds were characterized using XRD. Two most intense peaks were identified, corresponding to the (006) and (0015) planes which conform with the formation of bismuth selenide. Thin films of these compounds were deposited on Soda lime glass substrate by thermal evaporation method. Thin films were characterized by EDAX, SEM and RAMAN. Two clear vibration modes are observed corresponding to E_g^2 and A_{1g}^2 modes. Optical properties of thin films were also studied. Electrical band gap is found to increase with the increment in the amount of Bismuth in thin films.

Keywords: Bismuth selenide, Thin Film (TF), XRD, RAMAN, EDX, SEM, UV-VIS.

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1. Introduction

At present, thermoelectric materials (TE) are considered in many applications such as solid state power generating devices and refrigerating devices [1]. Bi_2Se_3 is a hot area of research because it is topological insulator which is an insulator but has surface conductivity. Bi_2Se_3 is a semiconductor belong to group V-VI [2]. Bismuth Selenide is environmentally friendly because ozone depleting elements like chlorofluorocarbons (CFCs) are not produced by it [3]. Recently by calculations and photoemission spectroscopy measurements on bismuth Selenide it is observed that it is a three dimension topological insulator with nondegenarate spins that makes it a perfect option in electronic and spintronics applications [4]. It is a well-known compound for its unusual anisotropic layered crystal structure, which increases the electrical conductivity of bismuth selenide [5, 6]. Bi_2Se_3 is a compound which has rhombohedral crystal structure. Bi_2Se_3 possess stacked layers of Bismuth and selenium that are held together by weak Van der Waals interactions. Each layer of bismuth selenide is one quintuple layer (QL) and five atoms are covalently bonded with each other along Z axis in the order of Se-Bi-Se-Bi-Se [7]. Bi_2Se_3 have applications in photosensitivity, photoconductivity and thermoelectric power devices because of their fantastic electrical and optical properties [8]. Therefore it is essential to determine the optical properties of bismuth selenide such as light absorption. According to R H Bari, Bi_2Se_3 is a narrow band semiconductor [9]. Band gap of Bi_2Se_3 lies between 0.2–0.3 eV in early report [10, 11]. Thin films of Bismuth Selnide have wide technological applications in solar devices, optoelectronic chemical devices [12], optical recording system and decorating coatings [13]. There are various methods to synthesize thin films including: chemical deposition [14], Magnetron sputtering [15], Successive ionic layer adsorption (SILAR) method [16], Molecular beam epitaxy [17, 18], Thermal evaporation [19] etc. In this communication, we report the synthesis of bulk bismuth selenide of different stoichiometries (0.123 to 0.309) by solid state reaction of bismuth and selenium. The aim of preparing four different samples is to investigate the effect of composition ratio on the structural and optical properties and to find out the best stoichiometry out of four different samples, which could be more applicable in field of photoelectronic and solar application. As in earlier literature only bi-layer thin films of Bi_2Se_3 having elemental ratio of 0.66 have been discussed. But in the present work, bulk bismuth selenide compounds and their thin films deposition by thermal evaporation process have been discussed. Achieved band gap values have been compared with previous literature to determine the best thin film which has lowest band gap, could be used in solar applications.Various characterizations techniques such as EDAX, RAMAN, SEM and optical microscopy were employed to study the films.

2. Experimental Analysis

2.1. Synthesis of Bismuth Selenide solid sample

Elemental precursors of Bi and Se of 99% purity were taken in quartz ampoules. After that ampoules were sealed maintaining the vacuum pressure of 10^{-6} torr. These ampoules were allowed to heat in muffle furnace at 850 °C for 15 minutes and then they were allowed to cool at room temperature. Finally, these ampoules were broken and samples were taken out and chunks were prepared for the preparation of thin films.

2.2. Synthesis of bismuth Selenide thin films

Thermal evaporation method is used for deposition of thin films from the prepared chunks. Thin films have been fabricated on Soda Lime Glass substrates. Prior to the deposition, all the substrates were rinsed in acetone and ultrasonically cleaned to remove the contamination from the surface of the substrates. Then hot bath were given at hot plate at the temperature of 70 °C with 80 rpm and lastly were rinsed in distilled water and were dried. Chunks of bismuth selenide prepared by solid state reaction method were used as a target for the preparation of thin films, employing the thermal evaporation method. The deposition chamber was evacuated to the vacuum of 10^{-6} torr and for uniform deposition substrates were rotated at constant rate of 8 rpm. Deposition has been done at constant rate of $\sim$2Å/s. Four different thin films of bismuth selenide with the thickness of 100 nm has been synthesized by using the four solid state reacted compounds. Further these thin films have been annealed at the temperature of 200°C. The phase and crystallography structure of solid samples of bismuth selenide have been studied by XRD. RAMAN spectra of thin films were also analysed. SEM and EDX were characterization have been performed to study morphological features and elemental composition respectively. Optical properties of thin films also have been analysed.

3. Result and discussion

3.1. X-Ray diffraction

To identify the crystallography of four solid samples of bismuth selenide, X-ray diffraction technique was used. Fig. 1 shows the XRD pattern of four solid compounds of bismuth selenide. From the XRD data it is clearly seen that two peaks are observed strongly along (006) and (0015) planes.

It means that bismuth selenide nanoparticles have the prominent growth in the direction of (006) and (0015) planes. The observed peaks are approximately matching with standard JCPDS data. The planes (006), (0015) correspond to theoretical data of Bi_2Se_3 (JCPDS file no. 33-214). Researchers observed peak corresponding to (006) plane and found that as bismuth increases in composition ratio, peaks shift towards high theta.

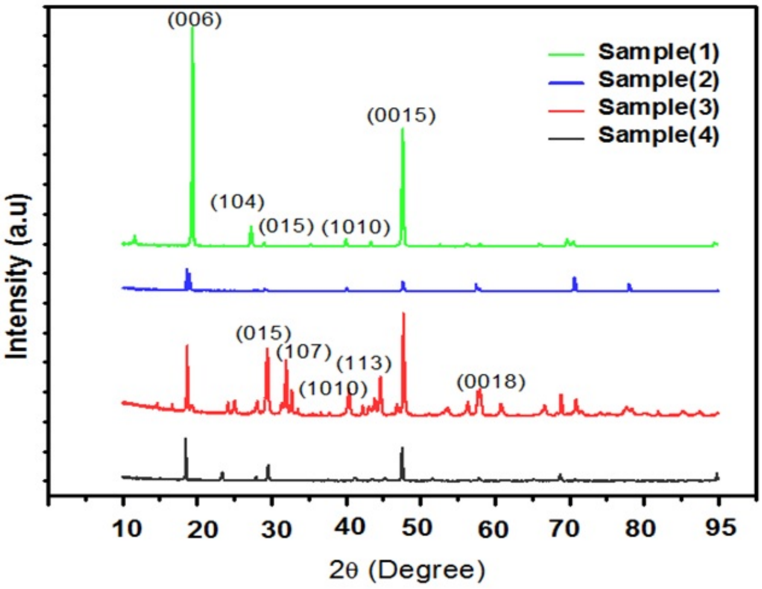

FIG. 1. XRD pattern of four solid compounds of bismuth selenide

3.2. Elemental analysis by EDX (ENERGY DISPERSIVE X-RAY SPECTROSCOPY) of as deposited bismuth selenide thin films

The elemental compositions of thin films were analyzed by energy X-ray spectroscopy (EDAX). Table 1 represents the results of elemental composition of bismuth and selenium present in as-deposited thin films (TF).

TABLE 1. Atomic percent and weight percent of Bismuth and Selenium in thin films

Sample Name	Wt%		At%		Bi/Se
Element	Bi	Se	Bi	Se	Atomic Ratio
TF–1	24.5	75.5	11.02	88.98	0.123
TF–2	31.57	68.3	14.85	84.15	0.176
TF–3	32.55	67.5	15.42	84.58	0.182
TF–4	45.1	54.9	23.63	76.37	0.309

The EDX results indicate the presence of bismuth and selenium in thin films of different stoichiometry. The ratio of Bi/Se is increases from TF–1 to TF–4.

3.3. SEM (Scanning Electron Microscopy)

The surface morphology of synthesized and annealed thin films of bismuth selenide have been studied against the SEM images. Fig. 2 shows the SEM images of as deposited thin film and annealed thin films. The data is extracted of grain size of five to six particles and presented the mean data of these values.

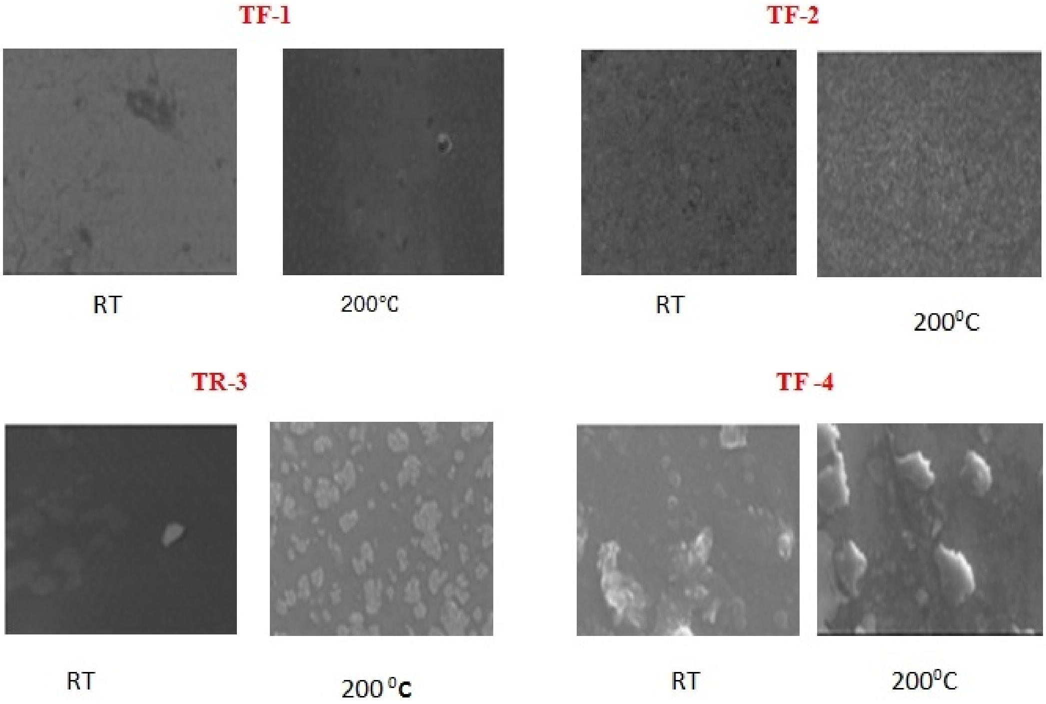

FIG. 2. SEM images of Bismuth Selenide thin films

From the SEM images it is clearly observed that annealing treatment affects the size of particle. It is profound that the grain size of thin films increased with the annealing treatment. A comparative analysis of grain size as a function of stoichiometric variation and annealing treatment has been disclosed in Table 2. The average grain size calculated using of different particle in single film. TF–1 to TF–3 the average grain size goes on decreasing. For films with higher concentration of bismuth ions, the growth occurs with multiple nucleation centers resulting in lower grain size, while for lower concentration of bismuth ions, comparatively lower nucleation centers gives higher grain size (20).

TABLE 2. Average grain size of particle in thin films for as-deposited and annealed thin films

Thin film (TF)	Average grain size RT thin films (nm)	Average grain size annealed thin films (nm)
(1)	41	100
(2)	60	97
(3)	28	54
(4)	124	137

This phenomenon is fully followed for TF–1, 2, 3. But TF–4 showed the higher grain size in comparison to other thin films and which may be due to some the formation of some other phases.

3.4. Raman Spectroscopy

Raman spectrometer is employed to study the vibration modes in thin films with wavelength of 532 nm (diode-pumped frequency doubled Nd:V) with better resolution. Theoretically there are four Raman active modes in bismuth selenide (Bi_2Se_3). There are two A_{1g} modes and two E_g modes in bismuth selenide (Bi_2Se_3). A_{1g} modes represent the atomic vibration along perpendicular to the layer and E_g modes are atomic vibration in plain [21].

Figure 3 shows the Raman spectrum of different four thin films of bismuth selenide. Clear Raman modes were observed at 131 cm^{-1} and 170 cm^{-1} corresponding to E_g^2 and A_{1g}^2 modes of Bi_2Se_3 [22]. The peaks result indicates that annealed thin films of bismuth selenide have better vibration modes than room temperature thin films. In annealed thin films A_{1g} mode is activated but in room temperature thin films it is not observed sharply. The low frequency modes E_g^1 and A_{1g}^1 not observed due to high Rayleigh background. The intense peaks of E_g^2 and A_{1g}^2 in bismuth selenide thin films reveal information of good quality.

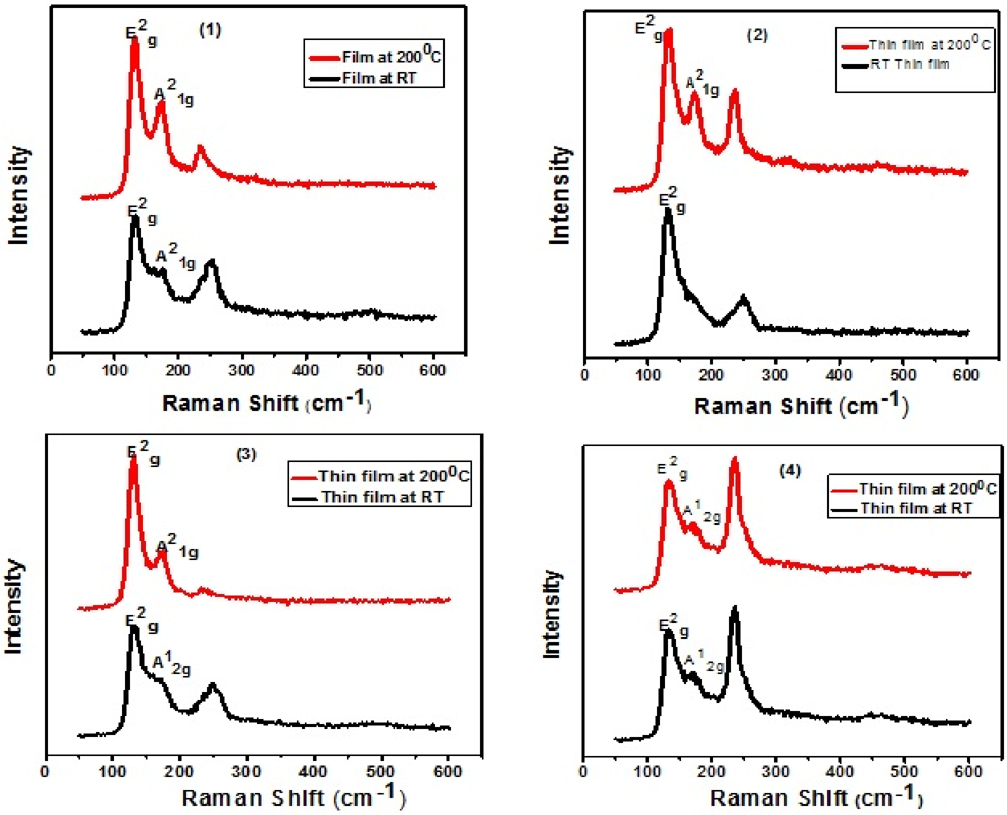

FIG. 3. Raman spectrum for thin films at RT and annealing temperature 200 °C for different four samples

4. Optical Studies

Optical features of bismuth selenide thin films have been investigated by using UV-VIS spectrophotometer [LAMBDA 750 (Perkin Elmer)]. Optical absorption spectra has been recorded at room temperature within the spectral range of 400 to 1600 nm for as- deposited and annealed thin films.

The variation in optical absorbance with wavelength is delineated in Fig. 4. The absorption coefficient (α) is a function of photon energy. The absorption coefficient (α) is calculated using Lambert law [23] as:

$$\alpha = (2.303A)/t,$$

where A is the optical absorbance and t is the thickness of the thin films. Thickness of all thin films is same of 100 nm. Absorption coefficient (α) provides the information about the type of optical transition occurred between conduction band and valence band of the sample.

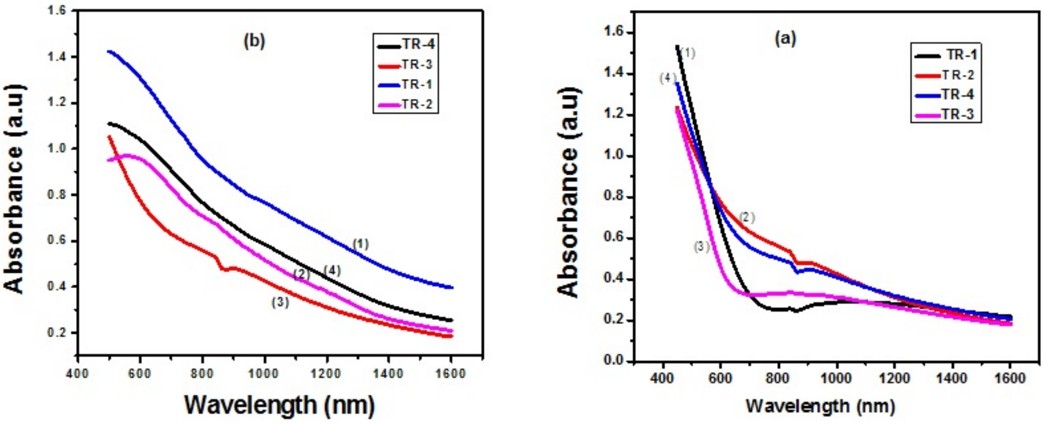

FIG. 4. Optical absorption of bismuth selenide thin films (a) as-deposited (b) annealed at 200 °C

The Tauc's equation for the calculation of direct band gap is given as:

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

where A is a constant which is related to the effective masses associated with the bands and E_g is band gap between conduction band and valance band. The index n is depends on the type of electronic transitions, for direct transition has n=1/2 or 3/2 while for indirect transition n=2 or 3, whether the transition are allowed or forbidden [24].

Tauc's plot for thin films have been presented in Fig. 5. The optical absorption coefficient is found to be in order of 10^{-6} m supporting the allowed direct band transition of the material. Allowed optical band gap is calculated by extrapolating the edge on energy axis ($h\nu$). The calculated band gap values are found within the range of 1.79–1.94 eV for as-deposited thin films and 1.33–1.4 eV for annealed thin films. The band gap values obtained for fabricated thin films in this work exhibited the lower values in comparison to the earlier data presented by researchers [25, 26]. Annealing treatment caused the decrement in the value of band gap. Further, the effect of stoichiometry variations is also detected in the values of band gap as it goes on decreasing with the increase in at% of Bi in the film composition. It may be due to smaller at% of Se; smaller would be the possibility of formation of localized levels in the forbidden gap. When the dislocation density is fairly high there is an increase in band gap of semiconductor material [27]. TF-1 to TF-3 band gap value decreases. Elemental value of Se in TF-4 is very low in amount in comparison to other. Because selenium is a semiconductor and very low amount of Selenium increase the band gap of TF-4.

The obtained values of band gap of bismuth selenide thin films are near the optimum value for photovoltaic conversion, which suggests that Bismuth Selenide thin films have promising applications in the field of solar energy and photoelectronics [28].

5. Conclusions

In previous work, researchers synthesized Bi_2Se_3 thin films having elemental ratio of 0.66, but in the present work, different thin films with different stoichiometric ratios (0.123 to 0.309) of Bi/Se have been prepared on glass substrate by thermal evaporation method. The foremost aim of the preparation of four different samples is to investigate the effect of compositional variation on the structural and optical properties and to find out the best stoichiometry out of four different samples, which could be more applicable in field of photoelectric and solar application. The EDAX of

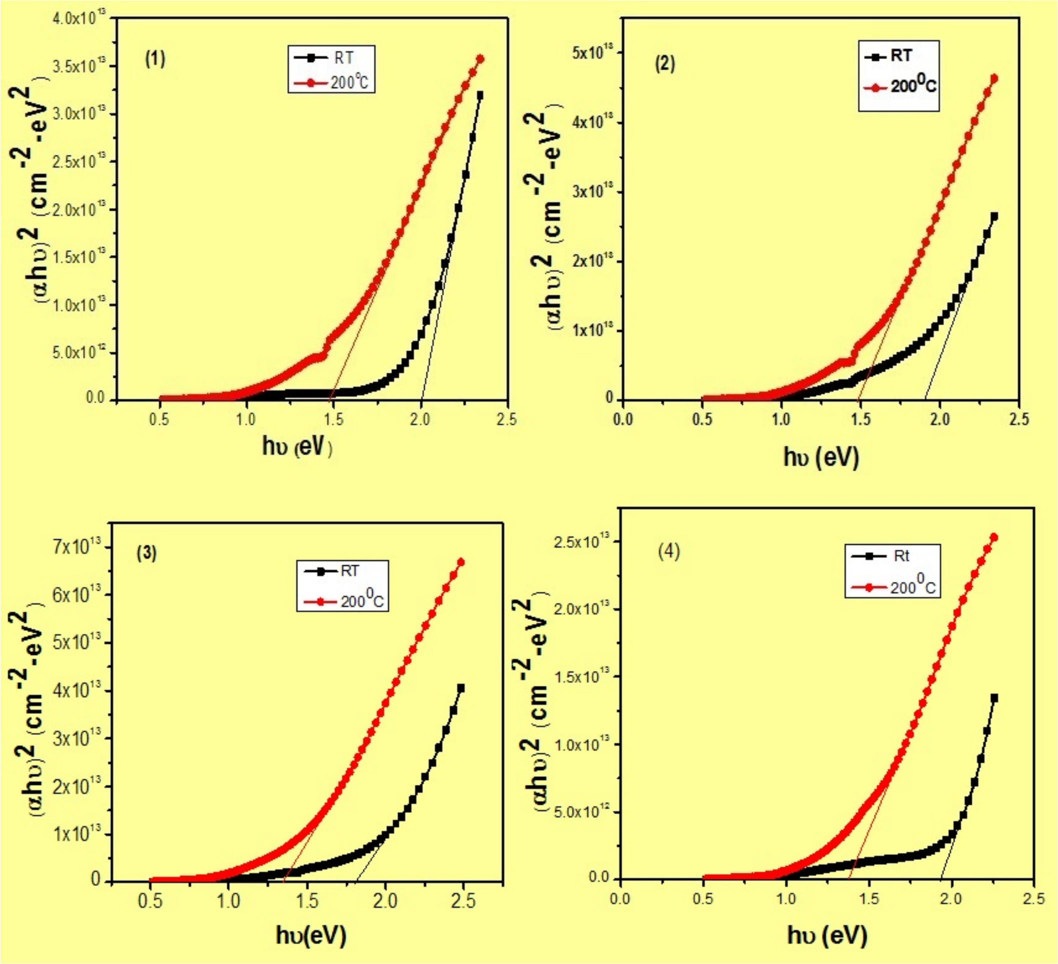

FIG. 5. Variation of $(\alpha h\nu)^2$ Vs $h\nu$ for as-deposited and annealed thin films

thin films indicated that the films were non-stoichiometric. The process of agglomeration becomes more prominent with the increment in of Bi/Se ratio. TF-1 which has elemental ratio 0.123 showed band gap 1.79, further insertion of Selenium in thin films caused a decrement in the band gap of thin films. But TF-4 which has high value of elemental ratio (0.309) of Bi/Se showed higher band gap value because of very low concentration of selenium. Out of four thin films, TF-3 which has elemental ratio 0.182 showed good optical results. Obtained band gap values of thin film reflect that these thin films used in field of solar energy. So that in many applications TF-3 could be used in place of Bi_2Se_3 thin film.

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