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Correlation of structural and optical properties in as-prepared and annealed Bi_2Se_3 thin films

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ABSTRACT

Bi_2Se_3 bulk alloys were synthesized using a standard mono-temperature melting process and used as source materials to deposit thin films on non-conductive super cleaned glass substrates by a vacuum thermal evaporation technique. Both bulk and thin-film samples were polycrystalline as confirmed by X-ray diffraction patterns. The film samples were subjected to the annealing process in air atmosphere at 250 and 300 °C for 3 h, aiming to boost the optical properties, in particular, to enhance the light transmission. The surface roughness, morphology and granular structure were investigated by atomic force microscope and scanning/transmission electron microscopes. The correlation between structural changes due to annealing and optical properties was observed. For a higher annealing temperature of 300 °C, the coefficient of transmittance increased reaching 80–90% in the IR range. Consequently, the absorption coefficient greatly decreased by annealing, especially for low photon energies. The optical band gap corresponds to the direct transition and increased notably by annealing from 1.51 to 1.83 eV. The spectra of optical parameters including the refraction index, coefficient of extinction and complex-valued dielectric function were deduced from the transmittance/reflection measurements to evaluate the effect of annealing. The energy loss functions were also estimated demonstrating that the volume and surface energy losses are of the same order.

1. Introduction

The investigation into the physical properties of binary chalcogenides (V_2VI_3) thin films is of continuing interest due to their unique electrical and optical properties enabling the development of prospective optoelectronic devices and thermo-electric modules (Manjulavalli et al., 2008). The other applications include television cameras and IR spectroscopy. Recently, Zhang et al. (2010) and Jie Yao et al. (2014) have discovered the topological insulating features in such materials, which has generated a renewed attention. It is well known that bismuth-based chalcogenides have a rhombohedral crystalline structure which is described in terms of layers made of five covalently bonded atomic planes, X-Bi-X-Bi-X. Such layer is referred to as a quintuple layer. In Bi_2Se_3 based chalcogenides, the quintuple layers are tied together with weak van der Waals forces forming a unique crystal structure. Yanping et al. (2016) have reported that two-dimensional (2D) ultrathin layered systems demonstrate tunable optical transition which provides exciting possibilities for potential applications in optics and photonics, including electrically-regulated optical filters, wide-range modulators, and smart windows.

3D materials with weak van der Waals bonds can be disassembled into quasi 2D systems in the form of thin flakes with the help of mechanical or chemical methods known as top-down processes (Shahil et al., 2012). The bulk of Bi_2Se_3 alloys with layered crystal structure which resembles the graphene structure is an attractive candidate to exploit "graphene-inspired" exfoliation methods to produce few quintuple layers. Liping et al. (2014) have demonstrated that owing to the weak bonding between the quintuple layers, the 2D-Bi_2Se_3 in the form of few-layer nanosheets can be prepared from 3D bulk alloys using liquid-phase exfoliation technique.

In this paper, we investigate the correlation between crystalline, structural, surface morphology properties and optical parameter spectra of Bi_2Se_3 films prepared by thermal evaporation technique. Post-preparation thermal annealing changes the structural characteristics and greatly influences the optical behavior.

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2. Experimental details

The bulk binary Bi_2Se_3 system was prepared by a standard melting method and was used as a source for preparing Bi_2Se_3 thin films. The melting process was conducted in high purity Bi and Se segments of purity grade, 99.99% (Aldrich Chem. Com). The starting elements were charged into the evacuated silica tube of 15 cm long and with the internal diameter of 0.8 cm. The tube was washed using distilled water and carbonized to avoid sticking the resultant ingot in its walls. After charging the precursors, the tube was evacuated down to 10^{-5} torr and then sealed to make a capsule. Melting was realized at a temperature of 1000 ℃ to synthesize good crystalline phases of Bi_2Se_3 compound due to the super-heating effect (the melting temperatures of Bi and Se are 271.5 and 221 ℃, respectively, and the Bi_2Se_3 phase forms at 705 ℃). To perform the required reaction, the alloying period was extended to about 12 h. Finally, the source materials of Bi_2Se_3 single-phase alloys with polycrystalline structure were attained.

Bi_2Se_3 thin films were deposited onto non-conductive glass substrates using vacuum thermal evaporation technique. To obtain uniform layers, the substrates were rotated during the deposition process and their temperature was maintained at room temperature. The film thickness was controlled by thickness monitor during the evaporation. The micro interferometer optical microscope (MUU10) was used to precisely measure the thickness of the prepared films. Its value was in the range of 2000 Å. The deposited films were annealed in air for 3 h at 250 and 300 °C to vary the structural and surface morphology properties and to understand their impact on the optical properties.

The crystalline structure of the prepared powder and thin film samples was investigated by X-ray diffraction (XRD). The Philips Xpert system with Cu-K_α monochromatic radiation source (1.5418 Å) was used. The diffraction data in the angular range of 10° - 60° were collected with a step width of 0.04°. The structural surface properties of the films (such as homogeneity, morphology) were fully characterized by microscopy methods including scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM). The optical properties were investigated with the help of double-beam Jasco spectrophotometer UV-VIS-NIR (Model V-670) allowing the measurements of transmittance and reflectance spectra in a wide wavelength range from 300 to 2700 nm.

3. Results and discussion

3.1. XRD characterization

The XRD patterns of Bi_2Se_3 samples in powder and thin film forms are given in Fig. 1. The patterns refer to polycrystalline hexagonal materials. A pure Bi_2Se_3 phase without any detected impurities can be seen in Fig. 1. A sharp peak at $2\theta = 18.639°$ demonstrates that a preferable crystallization growth is along the (006) orientation direction in the bulk Bi_2Se_3 system, whereas, the film grows along the (015) orientation at which the strongest peak was detected at $2\theta = 28.519°$. According to Liu et al. (2012), the crystal lattice parameters (a) and (c) of powders and films can be estimated using the hexagonal crystal structure equation for the main peaks:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (1)$$

In Eq. (1), d is the interplanar spacing (the space between crystallographic planes), h, k, and l are the Miller indices. The calculated values correspond to the standard values of hexagonal Bi_2Se_3 confirming that the film samples are hexagonal Bi_2Se_3. The standard card No: JCPDS 33–214 was used as a reference (Cosmas et al., 2012). In Table 1, the lattice parameters of Bi_2Se_3 in powder and thin film form are listed.

It is seen from Fig.1 that the diffraction peaks for Bi_2Se_3 thin films are much wider comparing to those of bulk materials which

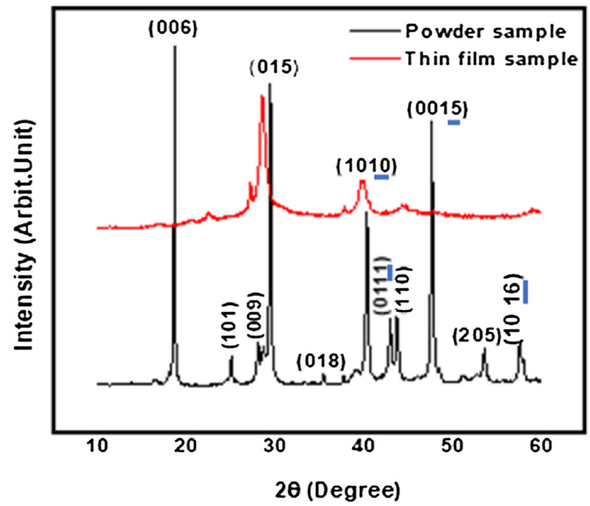

Fig. 1. XRD diffractograms of Bi_2Se_3 compound in powder and thin film forms.

Table 1
: Preferable plane of orientation, lattice parameters and grain sizes of Bi_2Se_3 samples in the form of powder and thin film.

Sample's form	Plane of orientation	Lattice Parameters (A°)	Crystallite size d_{XRD} (nm)
Powder	006	$a = b$ = 4.1396; c = 28.6360	41
Thin film	015	$a = b$ = 4.1401; c = 28.6401	13

corresponds to a smaller crystallite size, d_{XRD}. To calculate the value of d_{XRD}, the Scherrer equation was employed: $d_{XRD} = 0.89\,\lambda/\beta\cos\theta$, where θ is the Bragg angle, β is the corresponding peak broadening at half-maximum, and λ is the wavelength of the radiation source. The results are given in Table 1.

3.2. SEM characterizations

The SEM images of the source material (bulk alloy in a powder form) and as-deposited Bi_2Se_3 thin film are displayed in Fig. 2. The both types of samples consist of polycrystalline single-Bi_2Se_3 phase with a good structural form. Fig. 2a demonstrates that the powder samples are composed of individual particles of various sizes (the average value is about 700 nm). However, as seen in Fig. 2(b), as-prepared films have a smooth homogenous surface. The grains are greatly reduced (the average size value is about 45 nm) and dispersed uniformly.

3.3. AFM characterizations

The surface roughness and granular nature of the film samples were studied with the aid of Atomic Force Microscope (AFM). Fig. 3 depicts the 2D and 3D images revealing that the film surface is well-covered with Bi_2Se_3 grains. As seen in the 3D image, the grains have a hill-like shapes. The height of the surface grains was detected at a distance of 4 µm. In general, the AFM images reveal low values of surface roughness despite the hill-shaped grains. The surface roughness (mean square rms or Rq) of the film is found to be in the range of 45 nm. Therefore, the structure of the film is of a good quality.

3.4. TEM characterization

Fig. 4 displays TEM images of the as-deposited Bi_2Se_3 thin film. The data of Fig. 4a confirms that the film is formed of nano-crystalline grains of Bi_2Se_3 phase. To highlight the morphology, Fig. 4b shows a