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Impacts of thickness reduction and heat treatment on the optical properties of thin chalcogenide films

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ABSTRACT

Bi-based chalcogenides, in the form of thin crystalline films, were deposited at different thicknesses onto highly cleaned glass slides with the aid of vacuum thermal evaporation technique. The influence of thermal annealing on the optical properties of Bi_2Te_3-Bi_2Se_3 films at different thicknesses is investigated in this work. Wavelength dependence of the optical transmittance and reflectance was recorded, for the as-prepared and the annealed films, in the wavelength range from 350 to 2700 nm using a double beam spectrophotometer. Fundamental optical properties such as absorption coefficient and energy band gap were derived based on the measured spectra and film's thickness. We demonstrate in the present work that the synergy of annealing and thickness reduction can be exploited for light transmittance enhancements, and consequently for optoelectronic applications including transparent conductive electrodes.

1. Introduction

Due to its high thermoelectric properties, a considerable attention was devoted to the study of Bi_2Te_3 and based materials over the past years. Nevertheless, the attention was mainly dedicated to Bi_2Te_3 on its bulk form, and no much work was carried out on thin Bi_2Te_3 films. That is why, very few measurements on the optical properties of such system were reported [1]. In addition, Dheepa et al. [2] have studied the optical properties of thin Bi_2Te_3 films prepared by thermal evaporated, only over the wavelength range of 400–800 nm, they showed that the films are hexagonal and polycrystalline in structure.

Although annealing processes are known to enhance the transport properties [3], just a few number of reports, discussing the structural features changing by the effect of annealing and their relationship with transport properties on the Bi_2Te_3 thin films, were given in literature.

Practically, Bi_2Te_3 compound is usually obtained with directional solidification from melt or powder metallurgy processes. As a member of the V_2VI_3 binary chalcogenide compound semiconductors, it possesses very interesting properties which are quite suitable for applications in optoelectronic and electrochemical devices such as infrared sensors, heat pumps and high efficiency photovoltaic solar cells [4–8].

In terms of structure, Bi_2Te_3 is exactly similar to Bi_2Se_3. It is, naturally, designated in the form of stacked layers that are held together by weak van der Waals interactions showing laminated structure. Layers exhibit a quintuple structure in which five atoms are covalently bonded together along the z axis in the order of Te-Bi-Te-Bi-Te. Owing to that, it is possible to exfoliate bulk Bi_2Te_3 into few-layer nanosheets due to the weak interaction between layers [9,10].

Few-layered Bi_2Te_3 is recently considered as a highly promising and excellent material for technological applications. Dimensionality reduction beside material's final shape is quite an attractive recipe for applications due to reduced dimensions or surface area. Alongside with the applications in photosensitive devices, Hall-effect magnetometer, high-frequency power sensor thermopiles, wide band radiation detectors, and humidity sensors using the Seebeck and Peltier effects, it was found that addition of a third element such as Se to the binary Bi_2Te_3 thermoelectric system produces the best thermoelectric properties [11]. For this reason, nanocrystalline thin films were prepared by different methods such as electrochemical atomic layer epitaxy [12], successive ionic layer adsorption and reaction [13], precipitation in a capping agent [14] and thermal evaporation [15].

The main purpose of the present work is to report experimental results on the preparation of thin Bi_2Te_3-Bi_2Se_3 films by vacuum thermal evaporation technique and to study optical properties of the prepared films at different thicknesses before and after annealing treatments. In addition, the simultaneous effect of annealing process and thickness reduction on the structure and optical properties are studied as well.

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2. Experimental details

In our work, $Bi_2(Te_{1-x}Se_x)_3$ system was synthesized from pure Bi (99.999%), Se (99.999%) and Te (99.999%) elements. Mixtures of these pure elements were charged in vacuum-sealed quartz ampoules according to their stoichiometric formula, and then melted in a programmable furnace for 12 h at 1000 °C. The mixture was shaken several times to maintain uniformity and homogeneity. Finally, bulk crystalline alloys with single phase structure were obtained.

Based on the previously synthesized bulk alloy, corresponding Nano-crystalline $Bi_2(Te_{1-x}Se_x)_3$ films were deposited onto ultra-clean glass substrates, BK7 type; deposition process was carried out using thermal evaporation technique under high vacuum according to the following steps:

- Bulk sample was mounted on the dedicated holder.
- The sample heater was switched on when vacuum reached 3×10^{-6} mbar.
- The voltage variance was slowly rotated for the required deposition rate.

Substrates were kept at room temperature during the evaporation process and were rotated to obtain uniform layers, additionally, they were fixed at a distance of 20 cm away from the bulk sample evaporator. Thickness measurements were controlled by a thickness monitor, moreover; thickness was measured with the aid of micro interferometer optical microscope (MODEL MUU10) for much more precise determination. Different thicknesses were made for the purpose of studying the thickness reduction effect. Ultra-thin layers were prepared at thickness range between 100 nm and down to 15 nm. Thickness was calibrated and adjusted as a function of the sample's mass which we used in the evaporation process. Annealing process was conducted for all thicknesses of the films under the study at different temperatures for an annealing time of 3 h at air atmosphere in a well closed oven. Optical transmission and reflection spectra were measured after each annealing process at different thicknesses, using a double beam Jasco spectrophotometer UV–VIS–NIR (Model V-670) in the wavelength range of 350–2700 nm, a baseline was recorded prior to the actual measurements to calibrate the instrument for accurate results. Investigations were carried out on the annealed films under the work both separate and together with thickness reduced films.

3. Results and discussion

3.1. Crystal structure

X-ray diffraction (XRD) analysis, using Cu Kα radiation (λ=1.5406 Å), was carried out to study the structural properties of the thin films under the study. X-ray diffraction patterns for the as-prepared layers are shown in Fig. 1. In the given XRD diffractograms, sharpness of the structural peaks proves the polycrystalline nature of the investigated films [8]. Additionally, the appearance of different peaks on the diffractogram is due to the different orientations of the crystallite structures in the corresponding film sample. Notably, peaks appeared in the direction of the (015) orientation plane are the most intense peaks in all samples, indicating the growth favorability of the crystallites in this direction.

It is noteworthy that phases corresponding to all peaks, appeared on a certain particular diffractogram, were identified using the standard JCPDS data cards of Bi_2Te_3 and Bi_2Se_3 (Cards No. 15-0863 and 33–0214) [16]. The structure is identified in a hexagonal form with cell parameters a=4.13960 Å and c=28.63600 Å (space group: $R\bar{3}m$).

The average crystallite size has been calculated by means of the well-known Debye-Scherrer's equation:

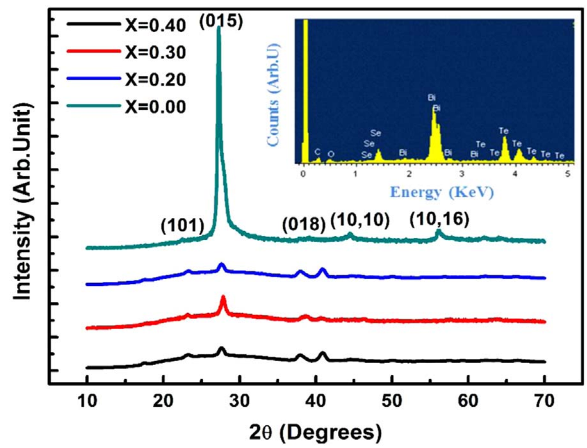

Fig. 1. X-ray diffraction (XRD) patterns of as-prepared $Bi_2(Te_{1-x}Se_x)_3$ layers.

$$D = \frac{K\lambda}{\beta_{hkl}\cos\theta} \quad (1)$$

Additionally, some important parameters characterizing layer's quality were derived using XRD patterns,

induced strain (Ɛ): $\varepsilon = (\boldsymbol{\beta}_{hkl}.\cos\theta)/4$, dislocation density (d): $d = \frac{1}{D^2}$ and the number of crystallites per unit area of the film's surface (N): $N=\frac{d}{D^3}$ were calculated using information given by diffractograms in the XRD patterns, values are presented in Table 1.

Inset of Fig. 1. illustrates the elemental composition analysis of the as prepared $Bi_2Te_{1.8}Se_{1.2}$ thin film (X=0.40), investigated using energy dispersive X-ray analysis (EDAX). Typical stoichiometry of the prepared composition is achieved. In addition, the chemical formula $Bi_2Te_{1.8}Se_{1.2}$ reveals a very nearly bulk material.

In other words, the bulk materials which were used as a source in the evaporation process showed compositional elements distribution as:

Bi – 40.12 at%.
Te – 42.43 at%.
Se – 17.45 at%.

Such ratios highlight an approximately ideal stoichiometric composition, which maintained in the structure of the corresponding deposited film's layers.

3.2. Surface morphology characterization

For much deeper study on the films' structure, surface morphology of the as-prepared films was scanned with the aid of scanning electron microscope (SEM). SEM micrographs are shown in Fig. 2. Obviously, all films under the study are featured with homogenous and smooth layer's surfaces, it can also be seen that substrates are well covered by $Bi_2(Te_{1-x}Se_x)_3$ materials. Additionally, highly crystalline films with extremely small grain size can be observed. It can be concluded from SEM observations that vacuum thermal evaporation technique is just suitable for the production of Nano-crystals based films.

3.3. Optical spectra of 200 nm thick films

Wavelength dependence of transmissivity and reflectivity of the as-prepared films is presented in Fig. 3(a), the figure indicates opaque materials over the whole wavelength range of the study, specially in the visible light region. Opacity in this region is due to the fact that all the light is absorbed at low wavelength (high photon energies). Nevertheless, transmittance showed obvious increase with wavelength increasing, due to low energies of photon (at high wavelength) and consequently no