Effect of thickness on structural properties of Bi$_x$Sb$_{2-x}$Te$_3$ thin films

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Abstract

Bi$_x$Sb$_{2-x}$Te$_3$ alloys with different ratios of Bi (x=0, 0.1, 0.3, 0.5, and 2) have been prepared. Thin films of these alloys were prepared using thermal evaporation method under vacuum of $10^{-5}$ Torr on glass substrates at room temperature with different deposition rate (0.16, 0.5, 0.83) nm/sec for thickness (100, 300, 500) respectively. The X–ray diffraction measurements for Bi$_x$Sb$_{2-x}$Te$_3$ bulk and thin films indicate the polycrystalline structure with a strong intensity of peak of plane (015) preferred orientation with additional peaks, (0015) and (1010 ) reflections planes, which is meaning that all films present a very good texture along the (015) plane axis at different intensities for each thin film for different thickness. AFM measurements for the thin films of Bi$_x$Sb$_{2-x}$Te$_3$, show that the grain size and the average surface roughness decreases with increasing of the percentage Bi for different thickness.

Key words

Bismuth tellurium, antimony tellurium, alloys, thin films, thermal evaporation, structural properties.

Introduction

many researchers recently resorted to study and expand both of clean and renewable energies, and tended to lessens the credence for energy that is produced from fossilized fuels (e.g. gas, oil, petroleum and coal etc), and also because of negatively effect of the surrounding environment to this type fuel and in turn by human, therefore the most frequent type of energy that researchers had been concerned since 1950. The energy that was producing by thermoelectric devices, these materials are able to make the thermal energy for direct conversion into electrical energy and vice versa [1]. Than in depending on the temperature process, so the thermoelectric materials can be classified to: Materials with high temperature above (900) K, as (SiGe) alloys, materials with mid-range temperature, as (PbTe) alloys, and materials with low temperature, as...
(Bi₂Te₃) and (Sb₂Te₃) based alloys for application at room temperature that belong for (V-VI) group [2].

In 1954 Goldsmid demonstrated the excellent thermoelectric properties of Bismuth Telluride, attributed mainly to the large mean molecular mass, low melting temperature and partial degeneracy of the conduction and valence bands of this V-VI chalcogenide [2]. Since that, bismuth telluride has been widely studied as a thermoelectric material with a narrow band gap, particularly in the temperature range around 300 K [2, 3]. Bi₂Te₃ or Sb₂Te₃ has a rombohedral structure with space group R3m, and the lattice is stacked in a repeated sequence of five atom layers: Te₁-Bi-Te₂-Bi-Te₁ along the c-axis, Te or and (Sb) and Bi layers are held together by strong ionic-covalent bonds (Te₁ or\ and Sb₁-Bi and Bi-Te₂ or \and Sb₂), while The Te₁ or\and Sb₁ bonds between cells are of the Van der Walls type and are extremely weak [4, 5]. Bismuth telluride compounds can be doped as either n- or p-type material by creating either a tellurium-rich composition or a bismuth-rich composition respectively [6].

In (2006) P.G.Ganesan et al have study thin films (Bi₀.₃Sb₀.₇)₂Te₃ for different thickness which deposited on a glass substrate by flash evaporation method in a vacuum 1*10⁻⁵ Torr. X-ray diffraction and Transmissin electron microscopic TEM analysis show that these films are polycrystalline even in the as-deposited state and the post-deposition annealing leads to grain growth. Electrical resistivity studies were carried out on these films as a function of T (300–450) k and film thickness (450–2000) Å [7]. In (2010) Pradyumnan et al have studied the Bi₂Te₃, Sb₂Te₃ and Bi₁Te₃, Sb₂Te₃ bilayer thin films various thickness which prepared by thermal evaporation method [8]. X-ray is use for the properties of the samples. Electrical studies is carried out using standard four probe method also the activation energy of each films. Thermoelectric behavior of each sample is determined at different temperature regions [8].

In (2015) Das et al. have study Bismuth Telluride films (Bi₂Te₃) were prepared using thermal evaporation technique in a vacuum 10⁻⁵ Torr on the glass substrate [9]. The study of electrical characterizations of Bi₂Te₃ thin films was carried out in the different thickness about 50-300 nm and temperature range 300-470 K. The electrical conductivity was found to increase with thickness of the films and temperatures. The activation energy was decreased with film thickness while the grain size was increased with the thickness. The Hall co-efficient, carrier mobility, carrier concentration, also studied. These results suggest that the investigated films are semiconducting in nature [9].

In (2018) A. M. ADAM et al have study Micro/ Nano-powders of the chalcogenide (Sb₁-x Biₓ)₂Te₃ system were composed by ball milling technique. The prepared powders were used as a source to production thin films with the aid of vacuum thermal evaporation methods. Crystal structure of the powders was studied by using XRD and SEM techniques, while the grown films were investigated via SEM and AFM analysis, which leads to an increased electrical conductivity and a reduced to the electronic thermal conductivity and the Seebeck coefficient [10].

The aim of this study is to produce thermoelectric Bi₁Sb₂-x Te₃ thin films using thermal evaporation technique, and look into the effectiveness of Bi percentage on the structural properties, in order to use it in the future to make thermoelectric devices, which were very effective to provide a clean
renewable energies to ensure a clean surrounding environment.

**Experimental**

To study the nano or micro structural properties of materials (Bulk or thin films), the X-ray diffraction technique (XRD) was used for this purpose. The reason of using X-ray diffraction (XRD) is attributed to a wavelength which is close to the distance between lattice points. The principle work of this technique depends on "Bragg law" which said the difference in the path between two beams is equal to the multiplying of the wavelength, and is given by Eq. (1) [11]:

\[ n\lambda = 2d \sin \theta \]  

where: \( n \) is integer representing the rank of overlap, \( \theta \) is Bragg angle, \( \lambda \) is wavelength.

The X-ray diffraction mode of amorphous materials appears as interfering and central wide halos, the sharp rings shaping points to the polycrystalline materials and the spots form show to a single crystalline materials. The peaks site offer information about structure and lattice orientation, the peaks width expounds the grain size of the crystals that were formed in the materials [12-14]. By using Scherer's formula we can calculated the grain size from XRD test as shown in Eq.(2) [15].

\[ G.S = \frac{0.9 \lambda}{\beta_{\text{FWHM}} \cos \theta} \]  

where: \( \beta_{\text{FWHM}} \) is Full Width at Half Maximum (FWHM).

To prepare the Bi\(_x\)Sb\(_{2-x}\)Te\(_3\) alloy with \( x = (0, 0.1, 0.3, 0.5, 2) \), in the beginning we have raw materials as powder. These materials are (Bi with purity 99.9, Sb purity 99.6, and Te purity 99.98) powders. All elements' weight in the alloy is obtain by a highly sensitive and precise balance and depended on the atomic weight, atomic mass, density of each element and the ratio of the alloys. The weight of each alloy is 3.5 g, the powders are mixed together and then located in a clean and dry quartz ampoules, then sealed under vacuum (1*10\(^{-3}\) Torr using a diffusing pump, after they are placed in a thermal oven at (900 °C) for 7 hr till they become homogeneous alloy at room temperature.

(CuK\(\alpha\)) radiation of wavelength (1.541Å), Current (30 mA), Voltage (40kV), Range (20000) counts/s, 10-80 (deg); Scan Mode: continuous scan, scanning speed: (5 deg /min). The Bragg’s condition for the diffraction can be show by the Eq.(1)

To determine the surface of the prepared Bi\(_x\)Sb\(_{2-x}\)Te\(_3\) thin film in nanoscale which can be measured using Atomic Force Microscope (AFM). To study and draw the surface topography we used this device in the field of nanotechnology; this microscope has the capability of analyzing up parts of a nanometer, this device exceeds the limit magnification optical microscopes more than (1000) times. In this study we used (AFM) system is (AA3000) type.

**Results & discussion**

The Results of the experimental investigations of Bi\(_x\)Sb\(_{2-x}\)Te\(_3\) alloys and thin films are interducing in this section. That structural measurements as : X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM) of Bi\(_x\)Sb\(_{2-x}\)Te\(_3\) alloys and thin films. The elements' concentration of Bi, Sb, and Te in the alloy of deferent values of \( x = (0, 0.1, 0.3, 0.5 \) and 2) have been determined by X-Ray fluorescence spectroscopy (XRF), it can be noticed that the compositional analysis of these alloys are in good stoichiometric percentage compared with the theoretical atomic percentages as show in Table 1.
Table 1: The theoretical and experimental atomic percentage of (Bi$_x$Sb$_{2-x}$Te$_3$) alloys.

| Alloys          | Elements | Atomic percentage % |   |   |
|-----------------|----------|---------------------|---|---|
|                 |          | Theoretical         | Experimental |
| Sb$_2$Te$_3$    | Sb       | 40                  | 41.6 |
|                 | Te       | 60                  | 58.4 |
| Bi$_{0.1}$Sb$_{1.9}$Te$_3$ | Bi       | 4                   | 5.09 |
|                 | Sb       | 36                  | 35.18 |
|                 | Te       | 60                  | 59.73 |
| Bi$_{0.3}$Sb$_{1.7}$Te$_3$ | Bi       | 12                  | 12.41 |
|                 | Sb       | 28                  | 28.17 |
|                 | Te       | 60                  | 59.42 |
| Bi$_{0.5}$Sb$_{1.5}$Te$_3$ | Bi       | 15                  | 16.25 |
|                 | Sb       | 25                  | 24.33 |
|                 | Te       | 60                  | 59.42 |
| Bi$_2$Te$_3$    | Bi       | 40                  | 41.11 |
|                 | Te       | 60                  | 58.89 |

Fig.1 shows the XRD patterns of Bi$_x$Sb$_{2-x}$Te$_3$ alloys at different Bi ratio (x=0, 0.1, 0.3, 0.5, and 2). It can be noticed that all samples have a polycrystalline structure with main diffraction peak to all alloys at (015) and the additional peaks; (0015), (006) and (1010), as seen in Table 2. These reflections' position have been compared with standard (JCPDS). From the results the most defraction peak appeared at (015) was shiftid towards smaller $2\Theta$ with increasing of Bi percentage, due to decrease in strain in the structure which happened because of Bi incorporation with lattice sites of Sb these results agrees with Tan [16].

Figs. 2-4 shows the XRD patterns of Bi$_x$Sb$_{2-x}$Te$_3$ thin films which deposited by thermal evaporation method at room temperature with different of (Bi) ratio of x=(0, 0.1, 0.3, 0.5, and 2) and different thickness (100 nm, 300 nm, and 500 nm). From these figures we noticed that all thin films have a polycrystalline structure, also we observed that a main preferred peak is (015), which shifted towards the smaller $2\Theta$ with increasing in Bi percentage, this behavior is attributed to the change in crystalline of the samples, which agreed with Sánchez [17] and Zhang [18]. As well as it can be noticed from the figure additional peaks which were corresponding to surface reflections planes (1010) and (101). The data of measuring (XRD) were approximately close to that listed in (JCPDS 96-7591) standards. All The results are listed in Table 3.

The values of crystallite size of Bi$_x$Sb$_{2-x}$Te$_3$ thin films were calculated from measuring the half width of the peak maximum intensity FWHM, and $2\Theta$ of the directions’ peaks by using Scherer's formula Eq.(2), [15] The grain size of Bi$_x$Sb$_{2-x}$Te$_3$ thin films, decreases with increasing of the Bi percentage for all thickness as shown in Table3, the grain size for various peaks of x-ray diffraction decreases when x value increases and this can be attributed to additive of Bi atoms in the structure of Sb$_2$Te$_3$ due to the different in atoms radius for Bi (1.6Å) and Sb (1.45 Å). This result is agree with Song [19] and Das [20].
Fig. 1: XRD pattern for Bi$_x$Sb$_{2-x}$Te$_3$ alloys at different ratio of Bi (0.1, 0.3, 0.5, and 2).
Table 2: The calculated values of interplaner distance (d-values), 2ϴ, G.S, and hkl for the Bi\textsubscript{x}Sb\textsubscript{2-x}Te\textsubscript{3} alloys.

| X  | (hkl) | 2ϴ(exp) (deg.) | d stand.(Å) | d Exp.(Å) | G.S (nm) | Aver. G.S(nm) | I/I\textsubscript{0} (a.u) |
|----|-------|----------------|-------------|-----------|----------|--------------|----------------|
| 0  | 015   | 28.33          | 3.157       | 3.146     | 31.87    | 30.33        | 100%           |
|    | 0015  | 44.65          | 2.030       | 2.027     | 27.18    | 35%          |                |
|    | 1010  | 38.35          | 2.356       | 2.349     | 31.94    | 43%          |                |
|    | 0.1   | 015            | 28.25       | 3.171     | 3.156    | 28.70        | 100%           |
|    | 0015  | 44.58          | 2.032       | 2.030     | 31.91    | 30.12        | 35%            |
|    | 1010  | 38.25          | 2.356       | 2.350     | 29.76    | 53%          |                |
|    | 0.3   | 015            | 28.22       | 3.171     | 3.154    | 27.00        | 100%           |
|    | 0015  | 44.41          | 2.032       | 2.031     | 30.60    | 27.88        | 28%            |
|    | 1010  | 38.19          | 2.356       | 2.354     | 26.06    | 23%          |                |
|    | 0.5   | 015            | 27.93       | 3.171     | 3.191    | 25.69        | 100%           |
|    | 0015  | 44.30          | 2.032       | 2.031     | 22.20    | 23.81        | 44%            |
|    | 1010  | 38.03          | 2.356       | 2.363     | 23.56    | 44%          |                |
|    | 2     | 015            | 27.62       | 3.230     | 3.226    | 28.75        | 100%           |
|    | 0015  | 44.35          | 1.996       | 2.019     | 31.19    | 29.11        | 31%            |
|    | 1010  | 37.89          | 2.360       | 2.372     | 27.39    | 31%          |                |

Fig.2: XRD patterns of Bi\textsubscript{x}Sb\textsubscript{2-x}Te\textsubscript{3} thin films with different Bi content with (x=0, 0.1, 0.3, 0.5, and 2) at thickness (100 nm).
Fig. 3: XRD patterns of Bi\(_x\)Sb\(_{2-x}\)Te\(_3\) thin films with different Bi content with (x=0, 0.1, 0.3, 0.5, and 2) at thickness (300 nm).
Fig. 4: XRD patterns of Bi$_x$Sb$_{2-x}$Te$_3$ thin films with different Bi content with (x=0, 0.1, 0.3, 0.5, and 2) at thickness (500 nm).
Table 3: The calculated values of (d-values), 2θ, G.S, and hkl for Bi₅Sb₂₋ₓTeₓ thin films at different thickness (100, 300 and 500 nm).

| Thickness T(nm) | X     | 2θ (Deg.) | d_{hkl} Exp.(Å) | d_{hkl} Std.(Å) | Phase    | hkl   | G.S (nm) | Average G.S(nm) |
|-----------------|-------|-----------|-----------------|-----------------|----------|-------|----------|-----------------|
| 100             | 0     | 28.181    | 3.1640          | 3.1578          | Hex.Sb₂Te₃ | (105) | 15.8     | 14.85           |
|                 | 0.1   | 28.463    | 3.1332          | 3.1578          | Hex.Sb₂Te₃ | (105) | 15.8     | 14.35           |
|                 | 0.3   | 28.322    | 3.1485          | 3.1578          | Hex.Sb₂Te₃ | (105) | 12.7     | 13.40           |
|                 | 0.5   | 27.805    | 3.2059          | 3.6925          | Hex.Bi₂Te₃ | (105) | 8.7      | 8.7             |
|                 | 2     | 27.570    | 3.2327          | 2.3773          | Hex.Bi₂Te₃ | (1010)| 9.4      | 10.6            |
| 300             | 0     | 28.265    | 3.1548          | 3.1578          | Hex.Sb₂Te₃ | (105) | 17.8     | 17.1            |
|                 | 0.1   | 28.396    | 3.1405          | 3.1578          | Hex.Sb₂Te₃ | (105) | 17.7     | 16.15           |
|                 | 0.3   | 28.354    | 3.1451          | 3.1578          | Hex.Sb₂Te₃ | (105) | 14.6     | 14.25           |
|                 | 0.5   | 27.478    | 3.2434          | 3.2274          | Hex.Bi₂Te₃ | (105) | 9.5      | 9.5             |
|                 | 2     | 27.259    | 3.2689          | 3.2274          | Hex.Bi₂Te₃ | (105) | 10.4     | 11.5            |
| 500             | 0     | 28.260    | 3.1554          | 3.1578          | Hex.Sb₂Te₃ | (105) | 18.3     | 18.45           |
|                 | 0.1   | 28.260    | 3.1554          | 3.1578          | Hex.Sb₂Te₃ | (105) | 17.6     | 17.65           |
|                 | 0.3   | 27.579    | 3.2317          | 3.2274          | Hex.Bi₂Te₃ | (105) | 14.4     | 15.05           |
|                 | 0.5   | 27.397    | 3.2527          | 3.2274          | Hex.Bi₂Te₃ | (105) | 9.0      | 11.06           |
|                 | 2     | 27.352    | 3.2580          | 3.2274          | Hex.Bi₂Te₃ | (105) | 12.0     | 11.73           |

The surface morphology of Bi₅Sb₂₋ₓTeₓ thin films which deposited on glass substrate at room temperature with different Bi percentage of (x) where (x=0, 0.1, 0.3, 0.5, and 2), and different thickness (100, 300 and 500 nm), which involving the average grain size and surface roughness, as shown in Figs.5-7. The average grain size of Bi₅Sb₂₋ₓTeₓ thin films decreases with increasing of the Bi percentage, as shown in Table 4, which involving the information about this analysis. The grain size is (95.31 nm) when x=0 and it decreases to (73.68 nm) when x=2 for thickness 100nm), also the grain size is (105.13 nm) when x=0 and it decreases to (76.52 nm) when x=2 for thickness 300 nm), while thickness (500 nm) the grain size is (108.85 nm) when x=0 which it decreases to (91.60 nm) when x=2. This may be seamed with the changing in atomic radius, and these results are agreed with those results which get from XRD analysis and also agree with Inad [21]. Also its observed that there is decreasing in surface roughness with increasing of Bi percentage, from
(0.755) nm at x=0 to (0.682) nm at x=2 for the thickness 100 nm, and from (1.56 nm) at x=0 to (1.41 nm) at x=2 for thickness 300 nm, while for thickness 500 nm the roughness decreases from (1.62 nm) at x=0 to (1.20 nm) at x=2. These results agree with Takashiri et al. [22].

Fig. 5: AFM images for Bi$_x$Sb$_{2-x}$Te$_3$ thin films at thickness (100 nm).
Fig. 6: AFM images for Bi$_{2}$Sb$_{2-x}$Te$_{3}$ thin films at thickness (300 nm).
Fig. 7: AFM images for Bi$_2$Sb$_{2-x}$Te$_x$ thin films at thickness (500 nm).
Table 4: The average grain size and roughness for Bi$_x$Sb$_{2-x}$Te$_3$ thin films deposited at room temperature with deferent zBi percentage ($x$=0, 0.1, 0.3, 0.5, and 2) and different thickness (100 nm, 300 nm, and 500 nm).

| Thickness T(nm) | X  | G.S (nm) | Roughness |
|-----------------|----|----------|-----------|
| 100             | 0  | 95.31    | 0.755     |
|                 | 0.1| 60.84    | 0.606     |
|                 | 0.3| 55.70    | 0.575     |
|                 | 0.5| 42.87    | 0.397     |
|                 | 2  | 73.68    | 0.682     |
| 300             | 0  | 105.13   | 1.56      |
|                 | 0.1| 82.64    | 0.785     |
|                 | 0.3| 63.80    | 0.476     |
|                 | 0.5| 61.23    | 0.373     |
|                 | 2  | 76.52    | 1.41      |
| 500             | 0  | 108.85   | 1.62      |
|                 | 0.1| 81.56    | 0.952     |
|                 | 0.3| 76.02    | 0.906     |
|                 | 0.5| 70.89    | 0.527     |
|                 | 2  | 91.60    | 1.20      |

Conclusions

The study of structural properties for Bi$_x$Sb$_{2-x}$Te$_3$ thin films with different Bi percentage (0, 0.1, 0.3, 0.5, and 2), and different thickness (100 nm, 300 nm, and 500 nm) which deposited by thermal evaporation technique at R.T. was concluded:
1-All thin films have a polycrystalline structure with main peak (015), which move toward the smaller 2θ.
2-The grain size of Bi$_x$Sb$_{2-x}$Te$_3$ thin films decreases with increasing of the Bi percentage for all thickness.
3-For the surface morphology of Bi$_x$Sb$_{2-x}$Te$_3$ thin films, the average grain size of Bi$_x$Sb$_{2-x}$Te$_3$ thin films decreases with increasing of the Bi percentage.

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