

Dependence of Structure and Optical Characterization of (Bi₂Te₃) Films Prepared by Flash Evaporation on Annealing Temperatures

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ABSTRACT

In this study Bi₂Te₃ stoichiometry alloy was fabricated by using melting method in the electric furnace at temperature (580 °C for 6h). Thin films (Bi₂Te₃) were deposited by flash technique under vacuum 10⁻⁵ Torr. The thickness measured of films was 500nm. the influence of annealing temperature (100 -200) °C was studied structure and optical properties of Bi₂Te₃ thin films. Structural properties for thin films of Bi₂Te₃ were investigated by XRD and AFM analysis. The XRD analysis of alloy show that poly crystalline phase for Bi₂Te₃ stoichiometry while the films prepared were amorphous at room temperature and phase transition to polycrystalline under annealing with preferred orientation at (015) corresponding to (2θ =27.639). FT-IR measured were studied for Bi₂Te₃ in range of (400-4000) cm⁻¹ under annealing temperature and this measured show that decreasing of E_g with increasing annealing temperature, this can be interpreted in term improved the crystal structure.

Keywords: Bi₂Te₃, XRD, AFM, FT-IR.

اعتماد الخاصية التركيبية والبصرية لغشاء (Bi₂Te₃) والمحضر بطريقة التبخر الومضي على درجات حرارة تلدنية

الخلاصة

في هذا البحث فأن سبيكة البزموت-تيليريوم والتي تم حسابها وزنيا تم تحضيرها بطريقة الانصهار في فرن كهربائي وعند درجة حرارية تصل الى 580م° ولمدة 6 ساعات. اما غشاء تلك السبيكة فقد تم تحضيره بطريقة التبخر الومضي وعند ضغط واطيء يصل الى 10⁻⁵ تور. والعامل الرئيسي والذي تمت دراسته في هذا البحث هو تأثير درجة حرارة التلدين على الخواص التركيبية والبصرية للغشاء ضمن المدى (100-200)م°. فبالنسبة للخواص التركيبية للغشاء فقد تمت دراستها باستخدام قياس نمط حيود الاشعة السينية وكذلك باستخدام قياس مجهر التركيب الدقيق لطبيعة سطح الغشاء. ان

تحليل حيود الاشعة السينية اكد بأن سبيكة البزموت-تيليريوم هي في طور متعدد التبلور اما الغشاء المحضر لنفس السبيكة فقد تبين انه في طور عشوائي عند درجة حرارة الغرفة ولكنه عند اجراء عملية تليدين الغشاء فإنه يتحول الى الطور متعدد التبلور. اما خ واص الغشاء البصرية فقد تمت دراستها باستخدام قياس تحويلات فورير للاشعة تحت الحمراء حيث تبين ان فجوة الطاقة البصرية لمادة الغشاء تتناقص بازدياد درجة حرارة التليدين .

INTRODUCTION

Bismuth telluride based alloys have been an attractive thermoelectric material widely used in cooling devices and proposed for energy conversion applications around room temperature. These thermoelectric devices can be almost maintenance free and downsizing because of no moving parts. It is possible to extend the applications of thermoelectric devices for their feature of downsizing. Micro-thermoelectric cooling is a suitable technique for the local cooling of micro-sensors and devices as it can be microelectronically integrated [1]. Micro-thermoelectric generating can supply small electric power to low power devices and actually have been equipped into wrist watches [2]. The primary candidate technology for downsizing of thermoelectric devices is to apply semiconductor-processing technologies including thin film fabrication. The key issue of micro-thermoelectric devices is how to fabricate thin films with high performance. The performance of thermoelectric materials depends on the thermoelectric figure-of-merit of the material, ZT [3], which is defined as

$$ZT = (S^2 * T) / (\rho * \kappa) \quad \dots(1)$$

where S is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal Conductivity, and T is the absolute temperature. The product (S^2/ρ) is defined as the power factor. The power factor should be maximized while the thermal conductivity should be reduced in order to achieve high efficiency thermoelectric materials. Recently, progress has been made in improving the figure-of-merit of thin film thermoelectric materials and a significant improvement in thermoelectric figure-of-merit may also be achieved by employing super lattice or quantum well structures [4]. There are presented many deposition techniques such as flash evaporated deposition [5], co-sputtering [6], pulsed laser deposition deposition [7], metal organic chemical vapor deposition (MOCVD) [8] and molecular beam epitaxy (MBE) [9]. Thus, although there are many deposition techniques, sufficient results for the stage of practical use have not been achieved yet because of higher production cost for expensive equipments or inadequate thin film properties.

In these deposition methods, we employ the flash evaporated deposition method as the fabrication of bismuth telluride based alloys thin films. On the other hand, the performance of the thin films is relatively low without annealing. In fact, annealing processes are known to enhance the transport properties [10]. However, there are few reports of linking a structural feature by the effect of annealing and that of transport properties on the thin films fabricated by flash evaporated deposition. The shape of the

absorption edge in the semiconductor Bi₂Te₃ has been determined from transmission measurements on cleavage sections. The edge is of the form expected for indirect transitions, but an interpretation in terms of phonons characterized by a single energy is not applicable. A brief study of anisotropy effects is included. The energy gap at room temperature is close to 0.13 eV.[11]

Experimental and Measurement technique

Bi₂Te₃ alloy were prepared by addition Bi element with Te element with chemical ratio, into very clean quartz tube, this tube were closed under vacuum 10⁻² Torr. The first quartz tube which contain Bi, Te and was heated up to (580°C for 6 hours) with checking to be sure that there is complete mixing and homogeneity for each compound. The Bi₂Te₃ film of thicknesses (500 nm), were prepared using flash thermal evaporation under vacuum 10⁻⁵mbarTorr using coating unit of type Edwards E 306 onto well-cleaned glass substrates at 27 °C. Bi₂Te₃ thin film formed by a flash thermal evaporation under a vacuum of 10⁻⁵ mbar. The stichometry of this compound was measured using Atomic absorption test where the weight of the alloy Bi₂Te₃ was 5gm which 2.609gm for and 2.395gm for Te . Bi₂Te₃ thin films were grown by a flash thermal evaporation method. Our schematic of our experimental flash evaporated deposition set up is illustrated in Fig. 1. Which deposited on a flat cleaned glass substrates for the structural properties and quartz substrates for the optical properties with a flash thermal evaporation method. The structure of these powders and thin films were carried out using X-Ray Diffraction (XRD) of type Shimadzu XRD-6000, Japan, with wavelength (0.15425 nm) of CuKα1. The XRD measurements were in the angle range from 2θ(20° - 60°). The optical transmittance for this film was measured using FT-IR spectrophotometer Jasco (V-570) in the range of wave length (190 – 2500 nm). The effect of annealing temperatures are studied on the structural and optical properties of Bi₂Te₃ thin film. Where the samples of thin film of Bi₂Te₃ annealed at different temperatures (273- 473)k.

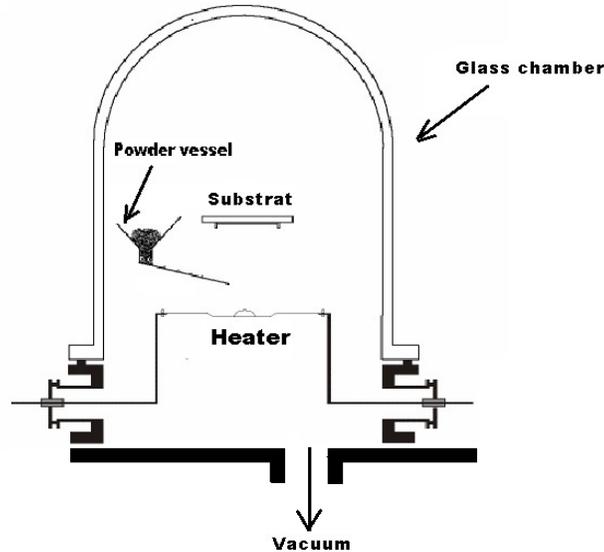


Figure (1).Schematic diagram of flash evaporated deposition

Results and discussion

The Atomic absorption measurement for the alloy of Bi₂Te₃ material have a nearly stoichiometry ratio because the ratio of elements of Bi₂Te₃ alloy was 53.51% : 46.39% respectively. Figure (1) shows the X-ray patterns of the Bi₂Te₃ alloy, from the figure (1) it is clear that alloy diffraction for this material have polycrystalline structure at room temperature [12] at thickness(500nm). Fig.2.show the XRD of Bi₂Te₃ thin film at different annealing temperatures(373 ,473)k, which describes the condition for constructive interference from successive crystallographic planes. The pattern indicated that annealing film in vacuum at (443k) for 1h was polycrystalline with a Hexagonal structure and the calculated lattice constant are a =4.43Å , c = 30.55Å, highly oriented crystallographic growth of Bi₂Te₃ thin films of 500 nm thickness as shown in figure(2). The crystal size "Grain Size " D, figure(2),was determined from Scherrer's formula.[13]

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \quad \dots(2)$$

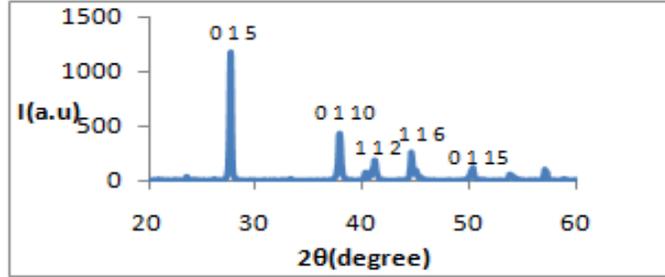


Figure (2) XRD of alloy of Bi₂Te₃

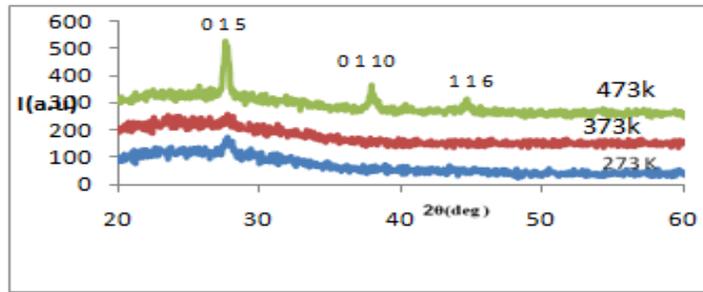


Figure (3) XRD of Bi₂Te₃ thin films annealed at different temperatures for 1h .

where: λ is the X-ray wavelength, $\lambda_{CuK\alpha}=0.15425$ nm, K: is the shape factor "constant" =0.95, β :is the (015) full width at half maximum intensity= 9.89×10^{-3} and θ : is the scattering angle or the Bragg's angle .This leads to Bragg's law, which describes the condition for constructive interference from successive crystallographic planes, From the calculated the values of the grain size D, are listed in Table (1).

Table (1): The relation between the crystal size "Grain Size " D with the film of Bi₂Te₃ at thicknesses 500 nm at different peaks intensities at (473k) .

d(A)	2θ Deg.	I _{int}	hkl	Grain size (A)	FWHM
3.2200	27.6630	100	015	176.9000	0.4625
2.3705	37.9254	34	1010	161.5000	0.5200

The as-grown thin film is not observed grains on this magnification of the micrograph and positional crystalanc , phases stand to growth . At annealing temperature of (473k), we confirm the grains where the size is approximately 178 nm. As annealing temperatures increase, the grain size of the thin films is enhanced. Finally, the grain size of the thin film reaches the same as the film thickness at annealing temperature of (473k). The as-grown thin film has weak and broad diffraction peaks that imply small grain size.. The diffraction peaks of the thin films are enhanced but the crystal orientation still remain random as annealing temperature increase. This clear in figure (3) which the AFM technique used to describe the effect of annealing temperature on morphology of the surface where the roughness of the surface is increase at thin film which annealing at (473K) a result of the diffusion of volatile Bi.

The energy band gap of the films was calculated with the help of transmission spectra, using the Tauc [14] relation:

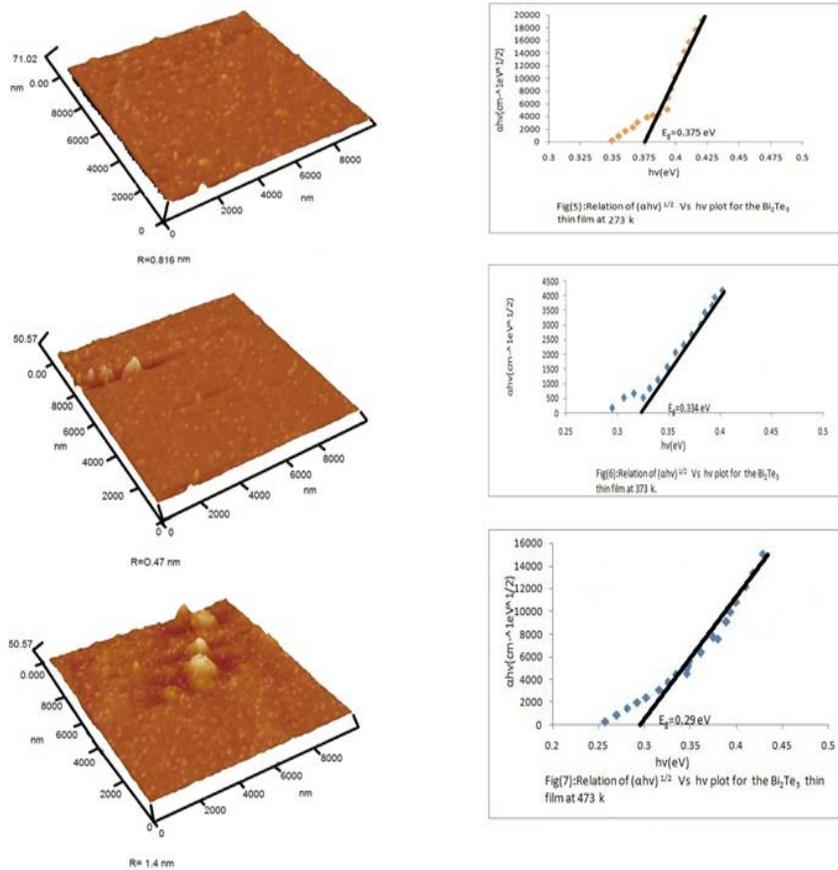


Figure (4).AFM images of Bi₂Te₃ film surface roughness.

$$\alpha hv = A(hv - E_g)^n \quad \dots(3)$$

where

- hv Photon energy
- α Absorption coefficient
- E_g Band gap
- A Constant
- n = 1/2 for indirect band gap
- n = 2 for direct band gap.

Figure(4) , $(\alpha hv)^{1/2}$ Vs hv plot, the optical band gap energy has been estimated at 273k and by the same methods the optical band gap energy at 373k,473k of the films and given in Table (2). The possible transitions in the Bi₂Te₃ thin films are indirect and allowed. It is observed from the table 2 the optical band gap shifts to a higher energy with increasing annealing temperature is due to the improvement of the crystallinity, thereby increasing the carrier concentration as determined from the Burstein–Moss effect[15].

Table (2): The relation between the optical energy gap and nealing temperatures of Bi₂Te₃thin film.

Annealing temperature (k)	Optical energy gap(eV)
273	0.375
373	0.334
473	0.29

CONCLUSIONS

The Bi₂Te₃ thin films grown by flash evaporation have been found to exhibit an amorphous nature. The annealing temperature of thin film leads to performance of structure to transform to hexagonal structure and the surface became rough. The possible optical transitions in these films are found to be indirect and allowed. The optical band gap decreases with an increase in annealing temperatures.

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