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Effect of vacuum annealing on structural, electrical and thermal properties of e-beam evaporated Bi_2Te_3 thin films

C. Sudarshan [a], S. Jayakumar [b,*], K. Vaideki [a], C. Sudakar [c]

[a] Thin Film Centre, PSG College of Technology, Coimbatore 641004, India
[b] Department of Physics, PSG Institute of Technology and Applied Research, Coimbatore 641062, India
[c] Multifunctional Materials Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

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ABSTRACT

Nanocrystalline thin films of a V-VI compound Bi_2Te_3 are fabricated with uniform thickness by e-beam evaporation at room temperature. The as-deposited films are stoichiometric, monophasic, highly strained and polycrystalline. We studied the effect of vacuum annealing (at a pressure of ~3×10^{-6} mbar) on composition, structure, optical and electrical properties of these films. It is observed that, as the annealing temperature increases (from 100 °C to 300 °C), the crystallites grow with a preferential orientation along (110) planes with slight increase in the crystallite size from ~14 nm to 30 nm. This is associated with the breaking of quintuple layers and rearrangement of crystallographic planes in the crystallites with Te rich surface emerging on vacuum annealing as evidenced from the XRD, Raman and high-resolution TEM studies. The direct bandgap (0.116 eV) of as-deposited Bi_2Te_3 changes from 0.092 eV to 0.113 eV on annealing at 100 °C to 300 °C, respectively. Interestingly, we observe a gradual change from a semiconductor to metallic behavior on annealing the samples from 100 °C to 300 °C. Such a transition from negative temperature coefficient (NTC) to positive temperature coefficient (PTC) is seen mainly due to the percolation of Te - rich crystallite surfaces, which evolve as the annealing temperature increases. While the films annealed at 200 °C and 250 °C shows a broad semiconductor to metallic transition at ~150 K and 200 K respectively, the thin films annealed at 300 °C are found to exhibit complete metallic behavior below room temperature. The electrical property and Seebeck coefficient studies with power factors in the range of ~4 to 12 × 10^{-4} W/K^2 m for films annealed above 200 °C suggest that the vacuum annealed Bi_2Te_3 thin films are favorable for thermoelectric applications.

1. Introduction

Bismuth Telluride (Bi_2Te_3) is a V-VI layered structure semiconductor with a rhombohedral unit cell (space group: $R\bar{3}m$) [1]. Bi_2Te_3 is highly anisotropic due to its layered structure and generally grows parallel to *c*-axis. Due to its narrow bandgap and unique thermoelectric characteristics at room temperature, Bi_2Te_3 is used in thermoelectric generators, thermo-coolers, and thermocouples [2–4]. It is also used as sensor and finds application in optoelectronics such as photoconductive targets for TV cameras and IR spectroscopy [5,6].

In recent times, a tremendous improvement in the bulk Bi_2Te_3 properties and its applications to various fields have been discussed [7,8]. However, in low dimensional structural forms the material properties differ and various studies are being carried out on this compound in thin films to improve their thermoelectric properties [9]. At small scale, *i.e.*, in thin films and nanostructures, there exist a great challenge to stabilize the structure and stoichiometry of Bi_2Te_3. Thin film fabrication is the most suitable technique that will be useful in semiconductor industry for producing low-dimensional thermoelectric devices. One of the main challenges that remain to be addressed is to fabricate high-quality thin films with excellent thermoelectric performance. Bi_2Te_3 thin films have been fabricated by various deposition techniques such as co-evaporation [10–12], evaporation [13,14], flash evaporation [15], co-sputtering [16], metal organic chemical vapour deposition (MOCVD) [17,18], pulsed electrodeposition [19], ion beam sputtering [20] and electrodeposition [21]. Due to volatile nature of Te most of these studies report the post annealing effects on structure and optical properties of Bi_2Te_3 thin films. Electron beam (e-beam) evaporation is one other promising technique to fabricate Bi_2Te_3 thin films that has scarcely been explored. Bi_xTe_y - based alloy thin films [22], influence of doping on the structural and optical properties of Bi_2Te_3 [23], and thermoelectric properties of Sb_2Te_3 [24] are few of the reports that have used the e-beam evaporation as the deposition technique. While there exist large volume of reports on the physical and thermoelectric properties of Bi_2Te_3 prepared by other techniques, more specifically by thermal evaporation, e-beam deposited thin films are scarce and would provide its own merits on properties of Bi_2Te_3 thin films. E-

* Corresponding author.
E-mail address: s_jayakumar_99@yahoo.com (S. Jayakumar).

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Table 1
The composition (Te:Bi ratio) of thin films deposited at various substrate positions (numbered 1 to 4 in Fig. 1) and e-gun powers are tabulated. The elemental concentration is determined with an uncertainty of 0.5 at.%.

Position of the sample	45 W Te:Bi (at.%)	67.5 W Te:Bi (at.%)	90 W Te:Bi (at.%)
1	51.4: 48.6	61.7: 38.3	70.2: 29.8
2	–	64.9: 35.1	–
3	–	70.1: 29.9	–
4	–	81.1: 18.9	–

beam evaporation uses source to substrate distances >10 cm in comparison <5 cm distance used in most of thermal evaporation and sputtering techniques. This avoids the unintentional substrate heating thereby minimizing the diffusion or evaporation of deposited atoms. In e-beam technique, bombarding the target material with an electron beam causes atoms from the source material to evaporate into the gaseous phase. These atoms solidify into a uniform thin coating on the substrate. The temperature of the substrate remains at ambient without significantly getting altered and the substrate surface damage is less due to impinging atoms, unlike in the sputtering that induces more damage because of the high-energy particles. Due to the high energy employed for the e-beam the source material is completely molten and made compositionally homogeneous before it vaporizes and gets deposited on to the substrate. The deposition rate in this process can be controlled to as low as 1 nm per minute to as high as few micrometers per minute. The material utilization efficiency is high relative to other methods and the process offers structural and morphological control of films.

In this paper we demonstrate that Bi_2Te_3 thin films can be deposited at room temperature with crystalline structure having near-stoichiometric composition by e-beam evaporation of bulk Bi_2Te_3 under optimized conditions. Further we have studied the post-annealing effect (under a pressure of ~3×10^{-6} mbar up to a temperature of 300 °C) on the structure, morphology, optical, and electrical properties of these films. We find that the crystallinity of the as-deposited Bi_2Te_3 improves with the annealing while the morphology and stoichiometry show slight changes. Interestingly, the temperature dependent resistivity measurements show that the as-deposited films are semiconductor-like with NTC response and vacuum annealing transforms the film to metal-like with a PTC on annealing to >250 °C for 1 h. The samples annealed at 200 °C and 250 °C exhibit a broad hump in the resistivity *vs* temperature plots at ~150 K and ~200 K respectively, indicating a semiconductor to metallic transition in these Bi_2Te_3 films. Samples annealed at 300 °C are completely metallic in the resistivity *vs* temperature response. We also discuss the electrical properties and show that the power factor of the films annealed below 200 °C is between 1 and 3×10^{-4} W/K^2 m, whereas the samples annealed at temperature above 200 °C exhibits an improved power factors in the range of ~4 to 12×10^{-4} W/K^2 m estimated from the Seebeck coefficients measured with an applied temperature gradients of 30 °C to ~150 °C.

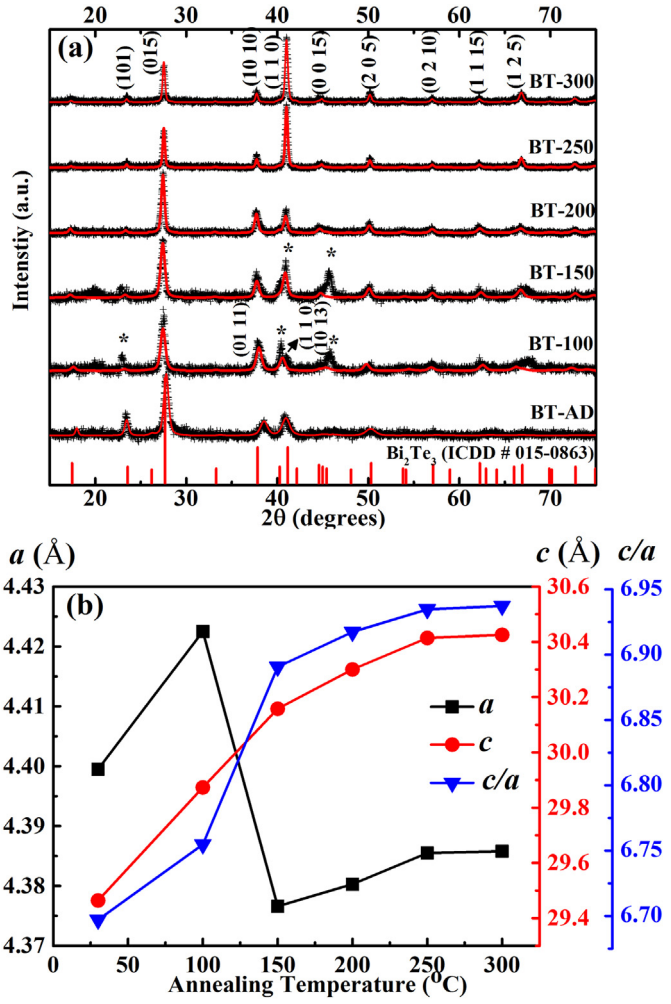

Fig. 2. (a) X-ray diffraction patterns of as-deposited (BT-AD) and annealed Bi_2Te_3 films (BT-T) along with the Rietveld refinement are given. Black symbols and red lines in the plot correspond to the measured intensities and calculated pattern. '*' in the patterns indicate impurity phase. (b) Lattice parameters (*a* and *c*), *c*/*a* ratio of as-deposited and annealed Bi_2Te_3 films are shown as a function of annealing temperature.

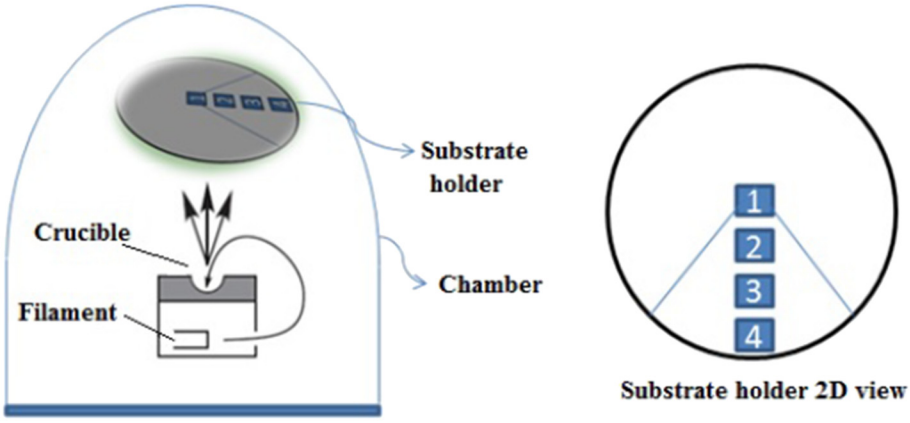

Fig. 1. Schematic of the e-beam evaporation system used to coat bismuth telluride thin films. The substrate holder shows four positions (numbered 1 to 4) separated by 3 cm.