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Thermoelectric properties of nanocrystalline Bi_3Se_2Te thin films grown using pulsed laser deposition

Le Thi Cam Tuyen [a], Phuoc Huu Le [b], Chih Wei Luo [c, **], Jihperng Leu [a, *]

[a] Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, 30049, Taiwan
[b] Faculty of Basic Sciences, Can Tho University of Medicine and Pharmacy, 179 Nguyen Van Cu Street, Can Tho, Vietnam
[c] Department of Electrophysics, National Chiao Tung University, Hsinchu, 30010, Taiwan

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ABSTRACT

This study reports the material and thermoelectric properties of *n*-type nanocrystalline Bi-Se-Te thin films grown using pulse laser deposition (PLD) with a Bi_2Se_2Te single crystal as the target. In order to optimize the transport and thermoelectric properties, Bi-Se-Te thin films are fabricated by maintaining the substrate temperature (T_S) between 200 and 350 °C and a helium gas pressure (P_{He}) from 0.027 to 86.7 Pa. Unlike the target, all deposited films unexpectedly exhibit Bi_3Se_2Te phase with highly *c*-axis orientation, because of the high re-evaporation rates of Se and Te at the elevated $T_S \geq 200$ °C. The estimated grain (crystalline) size ranges between 18.4 and 39.4 nm, and this monotonically increases as T_S increases. The Bi_3Se_2Te films demonstrate excellent electrical conductivities owning to the high carrier concentration in the order of 10^{20} cm^{-3}. A window of deposition conditions for high thermoelectric power factors (PF) is T_S of 250–350 °C and P_{He} of 40 Pa. The optimal PF is 8.3 $\mu W/cmK^2$ for the Bi_3Se_2Te film prepared at 250 °C and 40 Pa.

1. Introduction

Thermoelectric (TE) materials are of interest for applications as heat pumps and power generators [1–3]. The effectiveness of a thermoelectric material is defined by the dimensionless TE figure of merit, $ZT = S^2\sigma T/\kappa$, in which S, σ, κ and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity and the absolute temperature, respectively. The product $S^2\sigma$ is defined as the power factor (PF), which should be maximized. Meanwhile, thermal conductivity, κ should be minimized to obtain TE materials with high energy conversion efficiency [4,5].

In terms of the application of TE materials, thin films have a distinct advantage over the bulk form because: (1) the volume to be integrated into microelectronic systems is small, (2) they have a faster response time, and (3) they provide a greater heat pumping power density [1,6]. One of the approaches to further reduce the κ is to minimize the grain size of TE materials. Thus, nanocrystalline thin film appears to be a promising TE system. The κ values of nanocrystalline thin films were found to decrease with reducing grain size [5,7,8]. PLD is a versatile technique that enables the fabrication of TE thin films with high growth rates, multiple elements, and diverse structures and morphologies. Although nanocrystalline films can be prepared at low temperatures, these films usually possess poor σ values due to the presence of substantial residual crystal defects and imperfections. Recently, nanostructured and micro-/nano-crystalline films have been successfully fabricated using PLD by controlling the key deposition conditions such as the substrate temperature (T_S) and the ambient gas pressure [4,9–12]. Therefore, it is believed that TE films with desired nanoscale grain sizes and improved structural quality can be fabricated by controlling the PLD deposition conditions for higher values of T_S.

Bismuth chalcogenides (Te and Se) have been intensively studied for their high-performance TE properties [13–19] and their novel topological surface state [20–22]. In seeking new TE materials, this study re-examines the intermediate phases of bismuth chalcogenides which have rarely been studied [9,10,23]. In particular, the Bi-rich phase of Bi_3Se_2Te is of interest because it has a similar layered crystal structure to those of Bi_2Te_3-based materials for achieving poor κ along the *c*-axis [3,14]. In addition, the Bi-rich phase can create Bi semimetal nano-precipitates which further improves TE properties [24]. This study reports the TE properties of nanocrystalline Bi_3Se_2Te thin films prepared using PLD at various T_S of 200–350 °C and P_{He} of 0.027–86.7 Pa. The structural,

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* Corresponding author.
** Corresponding author.
E-mail addresses: cwluo@mail.nctu.edu.tw (C.W. Luo), jimleu@mail.nctu.edu.tw (J. Leu).

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morphological, compositional, and electrical properties of the films are also studied. An optimal-PF window as functions of T_S and P_{He} is determined.

2. Experimental details

Bi-Se-Te thin films were deposited on SiO_2/Si (100) substrates at T_S of 200–350 °C and P_{He} of 0.027–86.7 Pa (or 2×10^{-4}–6.5×10^{-1} Torr) using PLD. UV pulses (with pulse duration of 20 ns) from a KrF excimer laser ($\lambda = 248$ nm, repetition rate: 10 Hz) were focused on a single crystal Bi_2Se_2Te target with a pulse fluence of 6.25 J/cm^2; the target-to-substrate distance was 40 mm. The number of laser pulses was 9000 and deposition took 15 min. The average growth rate was approximately 0.6 Å/pulse. During the deposition, pure (6 N) He gas was introduced into the vacuum chamber, which was evacuated to a base pressure of 2.7×10^{-4} Pa (or 2.0×10^{-6} Torr) and maintained at a constant pressure, using a differential evacuation system. A 300-nm-thick SiO_2 layer was deposited on the Si (100) substrate using thermal evaporation to prevent any effects of the substrate on the subsequent electrical and Seebeck measurements.

The orientation and crystallinity of Bi-Se-Te films were determined using X-ray diffraction (XRD, Bruker D8) with Cu Kα radiation (λ = 1.5406 Å) in 2θ–ω and rocking-curve (ω-scan) configurations. Surface morphology and film thickness were examined using field-emission scanning electron microscopy (SEM, JEOL JSM-6500) through plane-view and cross-sectional images, respectively. Film compositions were also analyzed using an Oxford energy-dispersive X-ray spectroscopy (EDS) equipped with the SEM instrument at an accelerating voltage of 15 kV, a dead time of 22–30%, and a collecting time of 60 s. The atomic percentage of each film was determined by averaging the values measured at 5 (at least) distinct areas on the film's surface. Structural characterization at atomic scale was performed in a high-resolution scanning transmission electron microscope (HRTEM, JEOL JEM-ARM200F), operated at 200 kV. Cross-sectional TEM specimens were prepared using a standard mechanical thinning and Ar ion milling procedure. The chemical stoichiometry of a selected Bi-Se-Te thin film was characterized using X-ray photoelectron spectroscopy (XPS; ThermoVG 350) with the X-ray source (Mg Kα 1253.6 eV, 300 W). The binding energies obtained in the XPS analysis were standardized using C1s at 284.6 eV. XPS curve fitting was performed using the freeware XPSPEAK 4.1 with the Shirley background subtraction, and assuming a Gaussian–Lorentzian peak shape. The in-plane electrical conductivity, carrier concentration, and mobility were measured at room temperature using a Hall system (Bio-Rad HL5500 PC) with van der Pauw geometry. Seebeck measurements were performed at room temperature using a typical temperature-gradient approach [25]. The specimen was fixed on a homemade sample holder with a heater at one end to establish a small temperature gradient along the specimen. Two T-type thermocouples in contact to the specimen were used to measure both the temperature difference (in the range of 1.2–1.8 °C) and the voltage across the specimen under a temperature gradient. The Seebeck coefficient was then determined from the slope of the measured Seebeck voltage versus the temperature difference across the specimen.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the Bi_2Se_2Te target and films deposited at 40 Pa and T_S of 200–350 °C. The data shows that the target is a high quality Bi_2Se_2Te single crystal with *c*-axis orientation (JCPDS 01-073-7366). However, all films deposited at $T_S \geq 200$ °C exhibit variable patterns, in terms of both 2θ Bragg angles and the presence of two peaks at approximately 7.8° and 11.0° (Fig. 1(a)). Using the JCPDS Card No. 00-053-1190 and the hexagonal unit cell relationship ($a = 4.264$ Å, $c = 23.25$ Å), all XRD peaks were indexed and the phase of the films was identified as Bi_3Se_2Te. All of the deposited films are polycrystalline with highly (00l)-preferred orientation. Similar XRD results are observed for the films prepared at other P_{He} such as 0.027 Pa and 86.7 Pa.

Bi_2Se_2Te has a rhombohedral crystal structure (space group $R\overline{3}m$) that consists of hexagonally close-packed atomic layers of five atoms (quintuple layer, QL). These are arranged along the *c*-axis as follows: –[(Se/Te)–Bi–Se–Bi–(Se/Te)]– (see Fig. 1(b)), with lattice constants of $a = 4.18$ Å and $c = 29.14$ Å (JCPDS 01-073-7366). The outer atomic sites of a QL can exhibit a disordered occupation of Se/Te because of the weak van der Waals interaction between adjacent QLs [26]. The crystal structure of Bi_3Se_2Te is derived from an ordered stacking of Bi_2Se_2Te and Bi_2 building blocks, namely $(Bi_2)_m(Bi_2Se_2Te)_n$ ($m = 1, n = 2$) [23,27]. Fig. 1(c) shows that the structure contains double, covalently connected layers of bismuth –(Bi–Bi)– that lie between the QLs. The –(Bi–Bi)– strictly alternates with 2 QLs [23,27]. Notably, the layered crystal structures of Bi_2Se_2Te and Bi_3Se_2Te offer poor thermal conductivity along the *c*-axis [3].

Fig. 2 shows the *Ts*-dependent EDS compositions of the films deposited at various P_{He}. Compared to the stoichiometric elemental levels of the Bi_2Se_2Te target (i.e. 40 at.% Bi, 40 at.% Se, 20 at.% Te), the Bi-Se-Te films are Bi-rich and Se- and Te-deficient. For the 200°C-deposited films, a nonstoichiometric composition of Bi-rich (by < 6.0 at.%) and Se- and Te-deficient (by < 4.0 at.%) attributes to the formation of Bi_3Se_2Te phase. As T_S increases, Bi at.% increases but Se and Te at.% decreases toward the elemental compositions of the Bi_3Se_2Te phase (marked by the dashed lines). This is attributed to the fact that the vapor pressures of Se and Te are greater than that of Bi (~10^9 and ~10^6 times at 250 °C, respectively) [28]. The film compositions are found to be weakly dependent on the value of P_{He} (Fig. 2).

The nanograin size and microstrain of Bi-Se-Te films were estimated using the Williamson-Hall method [29] as defined by Eq (1):

$$\beta \cos \theta = \frac{K\lambda}{D_\beta} + 4\varepsilon \sin \theta \qquad (1)$$

where β is the full width at half maximum (FWHM) of the selected diffraction peak at 2θ, K is the Scherrer factor (~0.9), λ is the wavelength of the Cu K_α radiation (0.15406 nm), D_β is the nanograin size, and ε is the microstrain. The values of ε and D_β are respectively obtained from the slope and the intercept of the linear fitting in the plot of $\beta\cos\theta$ versus $4\sin\theta$. Fig. 3(a) presents T_S-dependent estimated grain sizes of the Bi-Se-Te films prepared at various P_{He}. The grain sizes are in the nanoscale range between 18.4 nm and 39.4 nm. As T_S increases from 200 to 350 °C, the grain size gradually increases: 20.9–39.4 nm for 0.027 Pa, 18.9–35.5 nm for 40 Pa and 18.4–35.7 nm for 86.7 Pa. Deposition at the lowest P_{He} of 0.027 Pa leads to a larger grain size. The grain size is weakly P_{He}-dependent in the range of 40–86.7 Pa. This phenomenon occurs because the mobility of adatoms is considerably limited by the adsorbed helium (at the grain boundaries), which in turn suppresses grain (or crystallite) growth in a high P_{He} regime and results in a smaller grain size [4,30]. Fig. 3(b) shows the effect of T_S and P_{He} on the microstrain for the films. The microstrain for Bi_2Se_2Te films grown at 200 °C is in range of 0.30–0.44%. This value decreases significantly for the Bi_3Se_2Te films prepared at $T_S \geq 250$ °C because an increase in T_S improves the ordering of atoms in the crystal lattice and reduces the concentration of crystal defects. This type of T_S-dependent microstrain is consistent with that for CdO thin films prepared on glass substrates [31].

The films' structure and crystallinity were determined using the