



Thermoelectric properties of bismuth-selenide films with controlled morphology and texture grown using pulsed laser deposition



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ABSTRACT

Polycrystalline, thermoelectric thin films of bismuth selenide (Bi_2Se_3) were grown on $\text{SiO}_2/\text{Si}(111)$ substrates, using pulsed laser deposition (PLD). Bi_2Se_3 films with highly *c*-axis-oriented and controlled textures were fabricated by maintaining the helium gas pressure (*P*) between 0.7 and 173 Pa and the substrate temperature (T_s) between 200 and 350 °C. The carrier concentration (*n*) of films decreased with increasing *P*, which was attributed to the increase of Se concentration from Se deficiency ($P \leq 6.7$ Pa) to stoichiometry to slight Se enrichment ($P \geq 40$ Pa). The Seebeck coefficient (*S*) was enhanced considerably because of the reduction in *n*, following the $S \sim n^{-2/3}$ relation approximately. The average grain size increased from approximately 100 to 500 nm when T_s was raised from 200 to 350 °C, resulting in enhanced carrier mobility (μ) and electrical conductivity (σ) and a reduced full width at half maximum of (006) peaks. The shape of grains transformed from rice-like at T_s of 200–250 °C to layered-hexagonal platelets (L-HPs) or super-layered flakes (S-LFs) at T_s of 300–350 °C. Films that were grown at 300 °C and 40 Pa and contained highly *c*-axis oriented L-HPs possessed the highest power factor ($\text{PF} = S^2\sigma$), which reached $5.54 \mu\text{W cm}^{-1} \text{K}^{-2}$, where $S = 75.8 \mu\text{V/K}$ and $\sigma = 963.8 \text{ S cm}^{-1}$.

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1. Introduction

Thermoelectric (TE) materials are used in appliances such as heat pumps and power generators [1–3]. The effectiveness of a thermoelectric material is defined by the dimensionless thermoelectric figure of merit $ZT = \sigma S^2 T / \kappa$, where σ , *S*, κ , and *T* are the electrical conductivity, Seebeck coefficient, thermal conductivity, and absolute temperature, respectively [4,5]. The quantity σS^2 is commonly used to represent the thermoelectric power factor (PF). For enhancing *ZT* value, an increase in PF together with a decrease in thermal conductivity is required. However, the coupling among thermoelectric parameters limits the efficiency and the practical applications of a TE material [5,6]. For example, *S* and σ ($= ne\mu$) are coupled through the relationship between *S* and *n*, expressed by $|S| \sim n^{-2/3}$ for degenerate semiconductors [6], or by $|S| \sim (1 + R)n^{-2/3}$ for semiconductors, where *R* is the scattering parameter [7].

The narrow-bandgap ($E_g \sim 0.3$ eV) semiconductor Bi_2Se_3 and other $A_2^{\text{VB}}B_3^{\text{VI}}$ -type compounds such as Bi_2Te_3 and Sb_2Te_3 are effective TE materials near room temperature [3,8]. A considerable amount of recent efforts to enhance TE performance has been devoted to the synthesis of Bi_2Se_3 nanostructures such as hexagonal flakes [9] and nanoflakes [10], using the solvo-thermal method and chemical bath deposition, respectively. However, few studies have reported the growth of Bi_2Se_3 thin films using pulsed laser deposition (PLD, a physical technique) or the characterization of the TE properties of such films. PLD is a versatile technique that controls deposition parameters and thereby enables films to be fabricated with multi-element stoichiometry as well as diverse structures and morphologies. Recent studies have revealed that the TE properties of Bi_2Te_3 films with distinct, controlled morphologies can be enhanced at certain ambient pressure (*P*) and substrate temperature (T_s) using PLD [11–13] or sputtering [14]. Bi_2Se_3 is more sensitive than Bi_2Te_3 to T_s because the vapor pressure of Se is higher ($P_{\text{Se}} > P_{\text{Te}} > P_{\text{Bi}}$ [15]), and therefore Bi_2Se_3 is often heavily *n*-type doped (because of the Se vacancy arising from Se evaporation) [16,17]. We postulated that the compositions and vacancies of the thin film can be controlled by changing *P*, and therefore we used Bi_2Se_3 , which is considered a suitable candidate material for investigating the incompletely understood effects of T_s and *P* on properties of the films.

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In this work, we systematically investigate the effects of P and T_s on the structure and morphology of Bi_2Se_3 thin films. The in-plane electrical and TE properties of the films were characterized and an optimized processing window of P and T_s conditions was determined for enhancing the PF of Bi_2Se_3 . The coupling of S and n has been demonstrated. Our results provide a comprehensive understanding of optimal PLD conditions and morphology of Bi_2Se_3 thin films for TE applications.

2. Experimental details

Bi_2Se_3 thin films were deposited on SiO_2/Si (111) substrates at T_s of 200–350 °C and P of 0.7–173 Pa using PLD. UV pulses (15–20 ns duration) from a KrF excimer laser ($\lambda = 248$ nm, 5 Hz repetition) were focused on a stoichiometric polycrystalline Bi_2Se_3 target with a pulse fluence of 3.8 J/cm²; the target-to-substrate distance was 50 mm. The number of laser pulses was 9000 and deposition took 30 min. The average growth rate was approximately 0.46 Å/pulse. During the deposition of Bi_2Se_3 films, pure (6N) He gas was introduced into the vacuum chamber, which was evacuated to a base pressure of 4×10^{-4} Pa and maintained at a constant pressure, using a differential evacuation system. An approximately 500-nm-thick SiO_2 layer was deposited on the Si substrate using thermal evaporation to prevent any effect of the substrate on the subsequent electrical and Seebeck measurements.

The orientation and crystallinity of Bi_2Se_3 films were determined using X-ray diffraction (XRD, Bruker D8) with Cu K α radiation ($\lambda = 1.5406$ Å) in 2θ - ω and rocking-curve (ω -scan) configurations. To collect detailed structural information on the films, digital images from a high-resolution (HR) transmission electron microscope (TEM) (Philips Tecnai F20), operated at 200 kV, were recorded using a Gatan 2k \times 2k charged couple device camera. The TEM specimens were prepared using a standard procedure of mechanical thinning and Ar-ion milling. 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 90 s. The atomic percentage of each film was determined by averaging the values measured at a minimum of 5 distinct areas on the film's surface. The in-plane electrical conductivity, carrier concentration, and mobility were measured at room temperature using a Hall system (Bio-Rad HL5500PC) with van der Pauw geometry. Indium balls were used to improve ohmic contact on the films' surface. Conductivity vs. temperature $\sigma(T)$ values were measured using a Physical Property Measurement System (PPMS, Quantum Design) between 2 K and 300 K, applying the standard 4-probe technique and using silver paste for the contacts. The in-plane Seebeck coefficient at room temperature was determined from the slope of the voltage difference vs. the temperature difference curve, based on a static temperature-difference method [19].

3. Results and discussion

3.1. Deposition temperature- and pressure-dependent crystal structure of Bi_2Se_3 films

Fig. 1a shows the XRD patterns of selected Bi_2Se_3 films deposited at distinct T_s (at 6.7 or 40 Pa for the optimal crystallinity of films in group I, 0.7 Pa for group II). The presence of dominant (00 ℓ) family planes (labeled from PDF#33-0214) clearly indicates that the films are highly c -axis oriented along the growth direction. Bi_2Se_3 has a rhombohedral structure with a space group

$D_{3d}^5 (R\bar{3}m)$ that can be described by a hexagonal primitive cell with three 5-atomic-layer thick lamellae (called quintuple layers, QLs) of $-(\text{Se}^{(1)}-\text{Bi}-\text{Se}^{(2)}-\text{Bi}-\text{Se}^{(1)})-$, in which the atomic layers are stacked in sequence along the c -axis [20], as shown in Fig. 1b. Neighboring QLs are held together by a van der Waals (VdW) bond of $\text{Se}^{(1)}-\text{Se}^{(1)}$, which is substantially weaker than the ionic-covalent bonds inside QLs such as $\text{Se}^{(1)}-\text{Bi}$ and $\text{Bi}-\text{Se}^{(2)}$ [21,22]. The weak $\text{Se}^{(1)}-\text{Se}^{(1)}$ bond leads to a c -axis-favored crystal orientation that has the lowest surface energy [23] and enables the preferential formation of sheet-like structures [24]. Notably, the layered crystal structure offers poor thermal conductivity along the c -axis [2,3].

The (012) and (024) peaks of pure bismuth (identified by PDF#85-1331) were observed at 27.3° and 56.3°, respectively, for the films deposited at 0.7 Pa, but these peaks were absent when $P \geq 6.7$ Pa, indicating Bi segregation (observed as high Bi enrichment in the 0.7-Pa films; Fig. 3). In addition to the dominant (00 ℓ) orientation, the films deposited at 350 °C showed the minor (10 ℓ) orientation of the BiSe phase (PDF #29-0246). The existence of the major Bi_2Se_3 and the minor BiSe phases in films deposited at 350 °C implies near-unity Se/Bi ratios in the films (more specifically, ratios ranging from 1.05 to 1.25; Fig. 3); the structure of these films may possess double, covalently connected layers of bismuth $-(\text{Bi}-\text{Bi})-$ intercalating in VdW gaps between QLs, and alternating with 2 QLs [12,20,25].

The mosaic structure and crystallinity of the films were determined from the full width at half maximum (FWHM) of the (006) X-ray rocking curve (Fig. 1c). FWHM decreased with increasing T_s , indicating improved crystallinity and better orientation between the crystallites (grains). At any given T_s , the FWHM also depended on P . The optimal deposition pressure (the pressure at which the smallest FWHM was associated with the optimal crystallinity) changed from 6.7 Pa to 40 Pa as T_s was increased from 200–250 °C to 300–350 °C. The effect of strain on FWHM was neglected because the films were up to at least three hundred nanometers thick. Thus, the present FWHM characteristics can be explained by considering the orientation and sizes of the grains. Large grain sizes reduce the probability of misorientation of the grains and therefore diminish FWHM [26]. Here, the average grain size increased from approximately 100 nm to 500 nm when T_s was increased from 200 °C to 350 °C (Fig. 2), leading to a drop in FWHM from approximately 10° to 2.7°. However, the narrowing of FWHM depended strongly on the orientation between crystallites (grains). Since the films deposited at 0.7 and 173 Pa were comparatively disoriented than those at 40 Pa, the FWHMs at 0.7 and 173 Pa were larger than at 40 Pa.

The detailed structure and orientation of the Bi_2Se_3 film deposited at 300 °C and 40 Pa were characterized using an HR-TEM (Fig. 1d). The P1, P2, and P3 regions, separated by the eye-guiding white lines (boundaries), revealed the granular-polycrystalline structure of the films. Moreover, P1 and P2 partly overlapped and the corresponding fast Fourier transform (FFT) of this overlapping region indexed by {003} patterns of [010] zone axis was performed from the dashed-square area (Fig. 1d, inset). The projected periods along the c -axes of both P1 and P2 were 9.60 Å, corresponding to (003) planes, which was close to the reported value of 9.55 Å in Ref. [27]. The c -axis angle between P1 and P2 was approximately 20°, which is the misorientation between grains (platelets) that accounts for the large value of FWHM in Fig. 1c.

3.2. Deposition temperature- and pressure-dependent microstructure of Bi_2Se_3 films

Fig. 2 shows the surface and cross-sectional morphology evolution of Bi_2Se_3 films prepared at various T_s in the 200–350 °C range and P in the 0.7–173 Pa range. At low pressure (0.7 Pa), films deposited at 200 °C were smooth and compact (SC), with

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