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Chapter 3

Thermoelectric and Topological Insulator Bismuth Chalcogenide Thin Films Grown Using Pulsed Laser Deposition

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/65898

Abstract

Bismuth chalcogenides have been intensively studied for their high-performance thermoelectric properties and their novel topological surface states, which could significantly benefit novel applications in fields such as TE devices, spintronics, and quantum computing. This chapter reports recent advances in pulsed laser deposition (PLD) for the growth of bismuth chalcogenide (e.g., Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_3$Se$_2$Te) thin films and their novel properties. It covers a wide range of fields such as thin film growth using PLD for fabricating polycrystalline and epitaxial films with different thermoelectric, nanomechanical, and magnetotransport properties as a function of the PLD processing conditions. Moreover, the proximity-induced superconductivities in Bi inclusions/bismuth chalcogenide thin films are also reported and discussed in detail.

Keywords: pulsed laser deposition, thermoelectrics, topological insulators, bismuth chalcogenides, superconductivity, magnetoresistance

1. Introduction

Bismuth chalcogenide thin films are of great interest because of the exciting properties of topological insulators (TIs) and their applications to thermoelectrics (TEs). These materials have been applied in integrated TE cooling devices working at near room temperature [1, 2]. TIs are exotic materials with an insulating bulk and topologically protected states on the surface which could be used in different applications, such as spintronics and quantum computing [3–6]. The topological surface states (TSSs) exhibit Dirac linear energy dispersion.
inside the bulk gap, spin-polarization by spin-momentum locking nature, and weak anti-localization (WAL) due to the strong spin-orbit coupling [3–6]. Thus, the WAL through magnetotransport studies has been widely used as a signature of TI materials [7–9].

For application purposes, thin film growth techniques for TE and TI materials are required. Among physical vapor deposition techniques, pulsed laser deposition (PLD) offers great versatility in growing polycrystalline and epitaxial thin films with high growth rates, multiple elements, and diverse structural morphologies for both fundamental studies and applications. The purpose of this chapter is to outline recent advances in the PLD growths of bismuth chalcogenide thin films with desired properties for TE/TI applications and fundamental studies.

2. Thin film growth using pulsed laser deposition (PLD)

Thin film growth consists of nucleation, growth, and coalescence (Figure 1a). In a physical vapor deposition, an extremely nonequilibrium process takes place at high supersaturations and at comparatively high concentrations of impure atoms [10]. Nucleation takes place at high supersaturations $S$ (defined as $S = p/p_e$, where $p$ is the vapor pressure of the deposited material evaporated from the source at temperature $T$ and $p_e$ is the equilibrium vapor pressure of the substrate material at temperature $T_S$). The incident vapor arrives at the surface of substrates and then forms small but highly mobile clusters or islands with uniform distribution. In this stage, the impinging atoms and subcritical clusters are incorporated and consequently increase their sizes, while the island density rapidly saturates. In the following stage, the islands are emerged via a coalescence phenomenon which is liquid-like for some cases, especially at high substrate temperatures. Coalescence leads to a decrease in island density and forms local denuding positions on the surface of substrates where further nucleation can then occur (Figure 1a) [11]. The sequence of film nucleation and growth events can be well appreciated in the transmission electron microscopy (TEM) images in Figure 1b–d [11].

2.1. Basic growth modes

For all phase transitions, the formation of thin films is characterized by the formation of nuclei and their growth. Depending on the interaction energies of substrate atoms and film atoms, any of three growth modes in Figure 2a–c can occur:

- 2D Frank-van der Merwe mode: layer-by-layer growth, in which the interaction between substrate and atoms of film is greater than that between adjacent atoms of film.
- 3D Volmer-Weber mode: separated islands form on the surface of substrates, in which the interaction between atoms of film is greater than that between a substrate and the adjacent atoms of film.
- Stranski-Krastanov mode: layer plus island, in which one or two monolayers form first and then grow individually.
Figure 1. (a) Schematics of thin film growth processes: nucleation, growth, coalescence. Transmission electron microscope images of (b) nucleation, (c) growth, and (d) coalescence of Ag films on (1 1 1) NaCl substrates. Corresponding diffraction patterns are shown.

Figure 2. Basic modes of thin film growth: (a) island in the Volmer-Weber mode, (b) layer by layer in the two-dimensional Frank-van der Merwe mode, (c) layer plus island in the Stranski-Krastanov mode. (d) Shadowing growth: a schematic of three-dimensional Monte Carlo simulations for oblique angle deposition [13].
After an initially random nucleation of islands on the surface of the substrates, the deposition on the top of the islands is faster than that in the valleys due to the oblique incident flux (the so-called shadowing effect) [12, 13]. Isolated columns are therefore formed on these islands during subsequent growths (Figure 2d) [13].

2.2. Epitaxy growth

Epitaxy refers to the growth of a single crystal film on top of a single crystal substrate. The deposited film is denoted as an epitaxial film or epitaxial layer. The growth is called homoepitaxy if the film and the substrate are the same material, and it is called heteroepitaxy if they are different materials. Epitaxial relationship is determined as: $(HKL) \| (hkl); [UVW] \| [uvw]$, where $(hkl)$ and $(HKL)$ are the Miller indices of the overgrowth plane and substrate at the common interface. The corresponding parallel directions in the overgrowth and substrate planes, denoted by $[uvw]$ and $[UVW]$, respectively, must also be specified.

2.3. Factors governing the epitaxy growth

The key factors governing epitaxy growths are structural compatibility, chemical compatibility, and growth temperatures.

- **Structural compatibility:** The structures of a film and a substrate should have good lattice matching in terms of crystal structures $(a_{\text{sub}}, a_{\text{film}})$ and lattice constants $(a_{\text{sub}}, a_{\text{film}})$, that is, small lattice misfit. Lattice misfit $f$:

  $$f = \frac{a_{\text{sub}} - a_{\text{film}}}{a_{\text{film}}} = \frac{a_{\text{sub}} - a_{\text{film}}}{a_{\text{film}}} \sqrt{2}$$

- **Chemical compatibility:** This includes chemical bonding and chemical diffusion.

- **Growth temperatures:** Good epitaxy growth is obtained at above or around the well-defined elevated substrate temperature ($T_s$). $T_s$ depends on the deposition rate, particle energy, and surface contamination. Generally, a higher temperature is recommended to reduce surface contamination by desorption (or enhance surface mobility) of atoms to reach the favorable sites and also enhance the diffusivity in deposition for favoring re-crystallization and defect annihilation.

2.4. Preparation of bismuth chalcogenide films by PLD

PLD is one of the most convenient thin film growth techniques that uses a high-intensity pulsed laser beam as an external energy source to ablate a target, form a plume, and then deposit thin films onto a substrate. Figure 3 shows a typical PLD system for preparing TE and TI thin films. A substrate is heated and maintained at a desired substrate temperature ($T_s$) using a thermocouple and a proportional-integral-derivative temperature controller. The thermocouple was
buried inside a stainless steel substrate holder, which is heated by a tungsten lamp just behind the holder. The pressure of ambient gas (He/Ar) can be fine-tuned by the needle valve. A KrF excimer laser beam (λ = 248 nm, pulsed duration of 15–20 ns, repetition rate in the range of 1–15 Hz, and fluence of 1–10 J/cm²) is guided by several UV mirrors and focused on a stoichiometric polycrystalline or a single crystal target (e.g., Bi₂Te₃, Bi₂Se₃, Bi₂Se₂Te) within the vacuum chamber by a UV lens. The target-to-substrate distance was 40 mm. During the deposition of Bi₂Se₃ films, pure (6N) He/Ar gas was introduced into the vacuum chamber, which was evacuated to a base pressure of 4 × 10⁻⁶ Pa (or 3 × 10⁻⁶ Torr) and maintained at a certain constant pressure (P), using a differential evacuation system.

Figure 3. Schematic illustration of a pulsed laser deposition (PLD) system. G: gauge.

The surface of substrates should be atomically clean and free from impurities because the contaminants can interact with the thin films being deposited and substantially degrade its quality and adhesion to the substrates. The presence of unwanted surface contaminants can also influence the growth and orientation of the films in an undesired manner. In the depositions for TE thin films, an approximately 300-nm-thick SiO₂ layer was thermally grown on the Si wafers (thickness 525 μm) for electrical isolation purpose. The wafers were cut into 1.5 cm × 1.5 cm substrates. The substrates were cleaned with acetone to dissolve any contaminants adhering to the surface of substrates such as grease and oils. This was followed by rinsing with methanol to remove any residues left behind after cleaning with acetone. Afterward, the substrates were rinsed in distilled water and dried with nitrogen flow. The substrates were then used for the deposition of TE thin films.

Here are some examples of PLD growth of TE films. For Bi₂Se₃ thin films, the depositions were at Tₛ of 200–350°C and helium ambient pressure (P) of 0.7–173 Pa. The number of laser pulses was 9000 and the deposition took 30 min. The average growth rate was approximately 0.46 Å/
pulse [14]. For the growth of Bi$_2$Te$_3$ thin films, $T_s$ was varied from room temperature (30°C) to 380°C and the Ar ambient pressure ($P_{Ar}$) was at 80 Pa. The number of laser pulses was 12,000 and the deposition took 40 min. The average growth rate was approximately 0.52 Å/pulse [15]. For the growth of Bi-Se-Te thin films, the depositions were at $T_s$ of 200–350°C and a helium ambient pressure ($P_{He}$) of 0.027–86.7 Pa. The number of laser pulses was 9000 and the deposition took 15 min. The average growth rate was approximately 0.6 Å/pulse [16].

3. Thermoelectric bismuth chalcogenide thin films

3.1. Crystal structures of bismuth chalcogenides

The crystal structures of bismuth chalcogenides (e.g., Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_3$Se$_2$Te) are usually described by a hexagonal cell consisting of 15 layers of atoms stacking along the $c$-axis with a sequence shown below [17], as shown in Figure 4a and b.

![Crystal structures of Bi$_2$Te$_3$, Bi$_2$Se$_3$, Bi$_3$Se$_2$Te](image)

A 5-atomic-layer-thick lamellae of -(Te$^{(1)}$-Bi-Te$^{(2)}$-Bi-Te$^{(1)}$)- or -(Se$^{(1)}$-Bi-Se$^{(2)}$-Bi-Se$^{(1)}$)- is called a quintuple layer, QL, in which the Te$_{^{(1)}}$-Bi and Bi-Te$_{^{(2)}}$ or Se$_{^{(1)}}$-Bi and Bi-Se$_{^{(2)}}$ are ionic-covalent bonds. Because of the weak binding (i.e., Van der Waals force) between Te or Se layers, bismuth chalcogenides could be cleaved easily along the plane perpendicular to the $c$-axis. It also induces the anisotropic thermal/electrical transport properties. For example, the thermal conductivity along the plane perpendicular to the $c$-axis (~1.5 W m$^{-1}$ K$^{-1}$) is nearly two times higher than that along the $c$-axis direction (~0.7 W m$^{-1}$ K$^{-1}$) [17, 18].

The crystal structures of Bi$_3$Se$_2$Te can be formed by ordered stacking of Bi$_2$Se$_3$Te and Bi$_2$ building blocks, that is, (Bi$_2$)$_m$(Bi$_2$Se$_3$Te)$_n$ $(m = 1, n = 2)$ [19, 20], in which the covalently connected double layers of bismuth (Bi–Bi) lie between two QL (Se-Bi-Te-Bi-Se) blocks (Figure 4c); the (Bi–Bi)
strictly alternates with two QL (Se–Bi–Te–Bi–Se) blocks [9, 20]. Figure 4d shows the typical XRD patterns of Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_3$Se$_2$Te thin films grown on SiO$_2$/Si substrates at $T_s = 300^\circ$C. They exhibit the dominance of (0 0 1) family planes of the rhombohedral phases of Bi$_2$Te$_3$ (PDF#82-0358), Bi$_2$Se$_3$ (PDF#33-0214), and Bi$_3$Se$_2$Te (JCPDS 00-053-1190), indicating that the films are highly c-axis oriented (i.e., textured films).

3.2. Introduction to thermoelectrics and applications

Thermoelectric materials are solid-state energy converters in which the combination of thermal, electrical, and semiconducting properties allows them to be used to convert waste heat into electricity or electrical power directly into cooling and heating [21].

3.2.1. The thermoelectric figure of merit (ZT)

The performance of the thermoelectric materials is often denoted as figure of merit $Z$ whose unit is K$^{-1}$ or $ZT$ with the dimensionless unit [17, 22].

$$\eta = \frac{T_b - T_c}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_c}{T_h}}$$

and for air-conditioning or refrigeration, the coefficient of performance is [23]

$$\text{COP} = \frac{T_b}{T_h - T_c} \frac{\sqrt{1 + ZT} - T_c}{\sqrt{1 + ZT} + T_c}$$

where $T_h$ and $T_c$ are the hot-end and cold-end temperatures of the thermoelectric materials, respectively, and $T$ is the average temperature of $T_h$ and $T_c$. Therefore, the enhanced $ZT$ value of TE materials is important to increase the COP for practical applications.
3.2.2. Conflicting properties in thermoelectric materials

Maximizing $ZT$ is challenging due to the interdependence of the TE parameters. An increased power factor $\alpha^2\sigma$ by optimizing the carrier concentration $n$ and/or a reduced lattice thermal conductivity $\kappa_L$ by introducing the scattering centers are necessary to enhance $ZT$ value. The dependences of these parameters with scattering factor $r$, carrier effective mass $m^*$, carrier mobility $\mu$, and their interconnectivity limits the $ZT$ to about 1 in large bulk materials [24].

The electrical conductivity ($\sigma$) and electrical resistivity ($\rho$) are related to $n$ through the carrier mobility $\mu$:

$$\frac{1}{\rho} = \sigma = n e \mu \quad (5)$$

The Wiedemann-Franz Law [2] states that the electronic contribution to the thermal conductivity is proportional to the electrical conductivity ($\sigma$) of the materials, with the relationship being

$$\kappa_e = LoT = n e \mu L T \quad (6)$$

where $e$ is electron charge, and $L$ is the Lorenz factor of $2.48 \times 10^{-8}$ J$^2$/K$^2$C$^2$ for free electrons and this can vary particularly with carrier concentration [2].

The kinetic definition of $\alpha$ is the energy difference between the average energy of mobile carriers and the Fermi energy [25]. An increase in $n$ leads to the increase in both the Fermi energy and the average energy, but the former increases more rapidly than the latter and thus results in a decrease in $\alpha$ value and a reduction factor of $\alpha^2 n$. Thus, in attempting to increase $ZT$ for most of the homogeneous materials, the carrier concentration ($n$) increases electrical conductivity ($\sigma$) but reduces the Seebeck coefficient ($\alpha$). For this reason, in metals and degenerate semiconductors (energy-independent scattering approximation), the Seebeck coefficient can be expressed as [2]:

$$\alpha = \frac{8\pi^2k^2}{3eh^3}m^*T\left(\frac{n}{3n}\right)^{2/3} \quad (7)$$

The high $m^*$ causes the Seebeck coefficient to rise according to Eq. (7). High $m^*$ materials generally possess low $\mu$ which limits the enhancement of power factor by $(m^*)^{3/2}\mu$. Noticeably, the defect scatters are not only the phonons but also the electrons which lead to reduce $\kappa_e$ as well as $\mu$. Therefore, the ratio of $\mu/\kappa_L$ determines the improvement in $ZT$ [17, 24]. Although the increase in the ratio is usually experimentally achieved through a greater reduction in $\kappa_L$ rather than that in $\mu$, some fundamental issues in this mechanism are not understood well [24].

**Figure 5** shows the compromise between large $\alpha$ and high $\sigma$ in thermoelectric materials that must be struck to maximize the figure of merit $ZT$. Meanwhile, the low carrier concentration...
will result in lower electrical conductivity with decreasing $ZT$. The $ZT$ and $PF$ peaks typically occur at carrier concentrations between $10^{19}$ and $10^{21}$ carriers per cm$^3$ (depending on the material system), which fall in between common metals and semiconductors, that is, the concentrations found in heavily doped semiconductors [2].

Figure 5. Maximizing the efficiency ($ZT$) of a thermoelectric device involves a compromise of thermal conductivity ($\kappa$, plotted on the $y$-axis from 0 to a top value of 10 W m$^{-1}$ K$^{-1}$) and Seebeck coefficient ($\alpha$, 0–500 μV K$^{-1}$) with electrical conductivity ($\sigma$, 0–5000 Ω$^{-1}$ cm$^{-1}$) [2].

3.2.3. Overview of thermoelectric applications

TE devices have unique features: no moving parts, substantially less maintenance, quiet operation, high power density, low environmental impact, and high reliability [26]. Commercial use has been made mostly from Peltier thermoelectric cooling (TEC) effect, such as in small refrigerator devices used for camping and outdoor activities, automotive climate control seats, and localized cooling at the hot spots of chips. Figure 6 gives an overview of the present and potential applications of thermoelectric generators (TEGs) [27]. Indeed, TEGs have been used for the power in miniaturized autarkic sensor systems, automotive waste heat recovery systems, ventilated wood stove, heating systems, water boilers, and heat recovery in industry.
3.3. Thermoelectric properties of polycrystalline Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_3$Se$_2$Te thin films with controlled structure morphology

Some typical HRTEM images of Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_3$Se$_2$Te grown using PLD are shown in Figure 7 [14–16]. HRTEM images performed on a high µ Bi$_2$Te$_3$ film with nanodisk-like morphology grown at 220°C are shown in Figure 7a. Clearly, the lower inset in Figure 7a shows the film with uniform thickness of approximately 295 nm and a SiO$_2$ layer with a thickness of 300 nm. It shows that projected period of 0.508 nm along the c-axis corresponds to the lattice spacing of the (0 0 6) planes. The highly (0 0 1)-orientated and crystallized structures of the film should facilitate the transport of charge carriers. The c-axis lattice constant of the Bi$_2$Te$_3$ film is 30.48 Å, which agrees closely with the value (30.44 Å) presented in JCPDS 82-0358. The other Bi$_2$Te$_3$ films grown at $T_s \geq 220^\circ$C also display similar HRTEM results.

For a Bi$_2$Se$_3$ film deposited at 300°C and 40 Pa, an HRTEM image taken at the boundary of three platelets (P1, P2, and P3) revealed the granular-polycrystalline structure of the films (Figure 7b). Moreover, P1 and P2 partly overlapped and the corresponding fast Fourier transform (FFT) of this overlapping region indexed by [0 0 3] patterns of [0 1 0] zone axis was performed from the dashed-square area (Figure 7b, inset). The projected period along the c-axes of both P1 and P2 was 9.60 Å, corresponding to (0 0 3) planes, which was close to the reported value of 9.55 Å in Ref. [28].
HRTEM images of a Bi$_3$Se$_2$Te film deposited at 250°C and 40 Pa are shown in Figure 7c and d. Nanocrystallites with sizes of 10–20 nm are clearly observed in Figure 7c, confirming the nanocrystalline type of the Bi$_3$Se$_2$Te films. The interplanar spacing of the Bi$_3$Se$_2$Te (0 0 5) planes in the nanocrystallites is approximately 0.464 nm. Therefore, the $c$-axis lattice constant is determined to be 23.2 Å, closely agreeing with the value of 23.25 Å for Bi$_3$Se$_2$Te bulk (JCPDS 00-053-1190). In addition, the white lines in Figure 7c indicate the orientations of the (0 0 5) planes. It is seen that the overall orientation of the crystallites is disorganized. Intriguingly, near the interface of the film and substrate, the film has some nanoinclusions with sizes of 12–17 nm, as shown in Figure 7d. The EDS analysis shows that these are Bi semimetal nanoprecipitates (the inset in Figure 7d). The lattice spacing of Bi nanoinclusions is ~0.32 nm, corresponding to the Bi (0 1 2) planes. It has been found that Bi nanoinclusions can lead to the enhanced Seebeck coefficient and reduced lattice thermal conductivity owing to the low-energy electron filtering and phonon scattering at the nanoinclusions, respectively [29–31].

Figure 7. (a) HRTEM images of a high carrier mobility ($\mu$) Bi$_2$Te$_3$ film with nanodisk-like morphology grown at 220°C and $P_{Ar}$ of 80 Pa. (b) HRTEM image of an optimized Bi$_2$Se$_3$ film deposited at 300°C and $P_{He}$ of 40 Pa. The inset shows the FFT patterns of the dashed-square area in the HRTEM image. (c and d) HRTEM images of the Bi$_3$Se$_2$Te film grown at 250°C and $P_{He}$ of 40 Pa. The white lines in (c) indicate the (0 0 5)-orientation of nanograins. Inset in (d): FFT patterns and EDS spectra performed at film and Bi nanoinclusion positions.
Figure 8a shows the $T_S$-dependent $\alpha$, $\sigma$, and $PF (= \alpha^2 \sigma)$ of some nanostructured Bi$_2$Te$_3$ films [15]. The $\sigma$ value gradually increased from $34.5 \pm 0.1$ to $814.3 \pm 1.5$ S/cm when $T_S$ was increased from 30 to 300°C, and then sharply decreased to $647.3 \pm 0.4$ S/cm at 340°C and $414.0 \pm 1.2$ S/cm at 380°C. The enhanced $\sigma (= 647.3 - 814.3$ S/cm) of the films grown at 220–340°C originated from the substantially enhanced $\mu$ because the $n$ exhibited a slight decrease [15]. Although the coupled relationship between $\sigma (= ne\mu)$ and $|\alpha|$ ($\sim n^{-2/3}$) generally constrains the concurrent enhancement of $\sigma$ and $|\alpha|$, a reduction in $n$ and a substantial increase in $\mu$ in the same optimal range of $T_S$ (= 220–340°C) could lead to high values of both $\sigma$ and $|\alpha|$. Consequently, the $PF$ of the stoichiometric Bi$_2$Te$_3$ films grown in the range of 220–340°C reached remarkably high values, ranging between $18.2 \pm 0.25$ and $24.3 \pm 0.44 \mu$W cm$^{-1}$ K$^{-2}$, whereas the $PF$ was low (≤$0.44 \mu$W cm$^{-1}$ K$^{-2}$) in the case of nonstoichiometric films deposited at $T_S \leq 120$ or 380°C (Figure 8a).
S and not the increase in $\sigma$. At intermediate pressures (40–93 Pa), the Bi$_2$Se$_3$ films remained stoichiometric or slightly Se-rich compositions, which in turn led to the reduced carrier concentrations and significantly enhanced the $\alpha$ values [14]. Thus, the PF of Bi$_2$Se$_3$ films grown at intermediate pressure was typically higher than the PF of films grown at a low or high pressure. The optimal value of PF was 5.54 ± 0.34 $\mu$W cm$^{-1}$K$^{-2}$ for the layered hexagonal platelet Bi$_2$Se$_3$ films deposited at 300°C and 40 Pa [14].

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<th>$\sigma$ (S/cm)</th>
<th>$\alpha$ (µV/K)</th>
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</table>

Table 1. Material, type, method, carrier concentration ($n$), mobility ($\mu$), electrical conductivity ($\sigma$), Seebeck coefficient ($S$), power factor ($PF = S^2\sigma$) of the optimal bismuth chalcogenide films in this study as compared to properties of Bi$_2$Te$_3$, Bi$_2$Se$_3$, Bi$_2$Se$_x$Te$_{1-x}$ bulk and films reported in the literature. All the selected values were recorded at room temperature.

The $T_S$ and $P_{16}$-dependent PF of nanocrystalline Bi$_2$Se$_3$Te films is further shown in Figure 8c. The films grown at 200°C only have PFs of 1.0–2.8 $\mu$W cm$^{-1}$K$^{-2}$. The PFs of the films grown at higher $T_S$ are significantly enhanced because of their high $\sigma$ values. Around $T_S = 250$–350°C and $P_{16} = 40$ Pa, a window for high PF is clearly observed. An optimal PF of 8.3 $\mu$W cm$^{-1}$K$^{-2}$ is achieved for a Bi$_2$Se$_3$Te film deposited at 250°C and 40 Pa.

Table 1 summarizes the transport and room-temperature TE properties of bismuth chalcogenides in the literature [14, 15, 32–39]. For PLD growths, the highly (0 0 1)-oriented layered Bi$_2$Te$_3$ films achieved a PF of 50.6 $\mu$W cm$^{-1}$K$^{-2}$ [39], and the layered compact polycrystalline
Finally, Figure 8d shows the $|S|$ vs. $\sigma$ plot for the list in Table 1. The solid curves denote different values of $PFs (= S/\sigma)$. It can be found that TE nanomaterials usually possess low $\sigma$ values due to the separating or voided structure morphology, but bulk and thin films have superior $\sigma$. Note, the significant reduction in thermal conductivity $\kappa$ is the key factor for employing nanostructured materials in the TE field.

4. Nanomechanical properties of Bi$_2$Te$_3$ and Bi$_2$Se$_2$Te thin films

Effects of helium ambient pressure (in PLD) on the nanomechanical properties of Bi$_2$Te$_3$ and Bi$_2$Se$_2$Te thin films have been investigated [9, 40]. The Bi$_2$Te$_3$ thin films were grown at $T_s$ of 250°C on c-plane sapphire substrates using excimer laser PLD with a power density of 5 J/cm$^2$, at a repetition rate of 2 Hz. The helium pressures in PLD growth varied from 2 × 10$^{-5}$ to 6.5 × 10$^{-3}$ Torr. Similarly, Bi$_2$Se$_2$Te thin films were deposited on Al$_2$O$_3$ (0 0 0 1) substrates at a fixed substrate temperature of 250°C and $P_{He}$ ranging from 2 × 10$^{-5}$ to 6.5 × 10$^{-1}$ Torr through PLD. The light source of the PLD system was a KrF excimer laser with $\lambda = 248$ nm, pulse duration of 20 ns, fluence of 7.0 J/cm$^2$, and repetition rate of 2 Hz. The target-to-substrate distance, the number of laser pulses and deposition time were 40 mm, 3000, and 25 min, respectively. The grown films had the average thickness of 200 nm (the average growth rate was $\approx$0.67 Å/pulse). Nanoindentation experiments were performed on a MTS Nano Indenter XP system with a three-sided pyramidal Berkovich indenter tip using the continuous stiffness measurement (CSM) technique [41]. The hardness and Young’s modulus of the Bi$_2$Te$_3$ and Bi$_2$Se$_2$Te thin films were determined from the load-displacement results through the analytical method proposed by Oliver and Pharr [42].

As shown in Figure 9a, the hardness monotonically increased from 2.92 ± 0.12 to 4.02 ± 0.14 GPa for Bi$_2$Te$_3$ films, and from 2.5 ± 0.2 to 3.0 ± 0.1 GPa for Bi$_2$Se$_2$Te films when $P_{He}$ was increased from 2.0 × 10$^{-5}$ to 2.0 × 10$^{-3}$ Torr. Similarly, the Young’s modulus of Bi$_2$Te$_3$ thin films was 106.31 ± 0.63, 115.51 ± 1.92, and 127.46 ± 9.21 GPa for $P_{He}$ at 2.0 × 10$^{-5}$, 2.0 × 10$^{-4}$, and 2.0 × 10$^{-3}$ Torr,
respectively. For $P_{\text{He}} > 2.0 \times 10^{-3}$ Torr, the hardness (Young’s modulus) of Bi$_2$Se$_2$Te films continues to increase with increasing $P_{\text{He}}$, namely 3.2 ± 0.1 GPa (105.2 ± 10.2 GPa) at $2.0 \times 10^{-1}$ Torr and 5.8 ± 0.2 GPa (188.5 ± 4.3 GPa) at $6.5 \times 10^{-1}$ Torr (Figure 9b).

The crystallite sizes ($D$) of the films were estimated using the Scherrer equation $D = \frac{0.9\lambda}{B\cos\theta}$, where $\lambda$, $B$, and $\theta$ are the X-ray wavelength, full width at the half maximum of the Bi$_2$Te$_3$ (0 0 15) peak or Bi$_2$Se$_2$Te (0 0 5) peak, and Bragg diffraction angle, respectively. The $P_{\text{He}}$-dependent $D$ of the Bi$_2$Te$_3$ and Bi$_2$Se$_2$Te films is shown in Figure 9c. The grain size increases monotonically from 11.0 to 20.0 nm for Bi$_2$Te$_3$ and from 16.1 to 20.5 nm for Bi$_2$Se$_2$Te with increasing $P_{\text{He}}$ from $2.0 \times 10^{-3}$ to $2.0 \times 10^{-1}$ Torr. In the nanoscale, grain size can affect significantly the mechanical properties of materials. The dislocation activities can be drastically suppressed in a polycrystalline material when the grain size is decreased, and thus the grain boundary sliding and/or grain rotations become the dominant deformation behavior, which in turn would lead to the manifestations of the inverse Hall-Petch effect [43]. Softening caused by grain boundary sliding is mainly attributed to large amount of defects in grain boundaries, which allow rapid diffusion of atoms and vacancies under stress [44]. Consequently, the plastic deformation of Bi$_2$Te$_3$ films should be dominated by the grain boundary sliding and/or grain rotation rather than the dislocation activity because of $D \leq 20$ nm [40], which is consistent with the results in Refs. [45–48].
In contrast, the 200-nm-thick Bi\(_3\)Se\(_2\)Te films with a range of 2.0 \(\times\) 10\(^{-5}\) to 6.5 \(\times\) 10\(^{-1}\) Torr exhibited the nanomechanical followed Hall-Petch relationship [44, 49]. The hardness and Young’s modulus of the Bi\(_3\)Se\(_2\)Te thin films monotonically increased with increasing \(P_{\text{He}}\) because of a corresponding decrease in grain sizes (Figure 9a–c). Figure 9d shows that hardness (H) increased linearly with \(D^{-1/2}\) (where \(D\) is the grain size of the Bi\(_3\)Se\(_2\)Te films in the nanoscale regime) which is the typical Hall-Petch relationship [44, 49]. This is because the multiplication and mobility of dislocations are hindered by reducing the grain size [44]. It is reasonable for the observed phenomenon when the present grain sizes ranged between 25.1 and 16.1 nm which is larger than the typical critical \(D_c\) of 10 nm [44, 49]. It is demonstrated that the hardness and Young’s modulus of the Bi\(_3\)Te and Bi\(_3\)Se\(_2\)Te thin films can be enhanced by proper selection of the ambient pressure in PLD growths.

5. Topological insulator bismuth chalcogenide thin films and their novel properties

5.1. The epitaxial growths of bismuth chalcogenide thin films

Topological insulator (TI), a new class of quantum matter, possesses insulating in bulk and robust gapless topological surface states (TSSs) in which the spin of the electron is locked perpendicular to its momentum by strong spin-orbit interaction [6, 50, 51]. TIs have been identified as promising materials for exploiting exciting physics and developing potential applications in optoelectronics, spintronics, and quantum computations [50–54]. Dirac fermions in TIs have also been studied by angle-resolved photoemission spectroscopy [55–57] or scanning tunneling microscopy [58, 59]. In magnetotransport studies, TSS can be studied by weak antilocalization (WAL) [4, 9, 60, 61] and Shubnikov-de Haas oscillations [3, 62].

Topological insulator bismuth chalcogenide thin films have been grown epitaxially on various substrates using PLD. Onose et al. reported the epitaxial growth of Bi\(_2\)Se\(_3\) thin films on InP (1 1 1) substrates (the lattice mismatch of 0.2%) [7]. A designed Se-rich target with an atomic ratio of Bi:Se = 2:8 was used to compensate for the issue of high doping carriers and to avoid unwanted Se-deficient phases. The pulsed laser power and repetition were 140 mJ and 10–20 Hz, respectively. The Bi\(_2\)Se\(_3\) films obtained a small full-width at half-maximum (FWHM) for the XRD rocking curve of (0 0 0 6) peak. The surfaces of the films are composed of triangular pyramids with step-and-terrace structures, reflecting the hexagonal symmetry of Bi\(_2\)Se\(_3\). The epitaxial relationship is Bi\(_2\)Se\(_3\) || InP (1 1 1) and Bi\(_2\)Se\(_3\) [1 1 0] || InP [0 0 1]. Le et al. reported the epitaxial growth of Bi\(_2\)Se\(_3\) films on SrTiO\(_3\) (STO) (1 1 1) substrates using PLD at \(T_s\) of 300 and 350°C [63]. The PLD conditions were the pulse fluence of 3.7 J/cm\(^2\), helium pressure of 40 Pa (300 mTorr), and repetition rate of 2 Hz. The laser source was KrF excimer laser (\(\lambda = 248\) nm, duration 20 ns). By comparing the Bi\(_2\)Se\(_3\) [0 1 5] and STO [2 0 0] diffraction peaks, the epitaxial relationship between the film and substrate was determined to be Bi\(_2\)Se\(_3\) || STO (1 1 1) and Bi\(_2\)Se\(_3\) [1 1 0] || STO [1 1 0] [63].
Figure 10 presents the PLD epitaxial growths of $\text{Bi}_2\text{Te}_3$, $\text{Bi}_2\text{Se}_3$, and $\text{Bi}_3\text{Se}_2\text{Te}$ thin films on large-misfit substrates [9, 53, 64]. The PLD conditions for growing $\text{Bi}_2\text{Te}_3$ films on STO (1 0 0) were as follows: substrate temperature of 300°C; helium ambient pressure of 40 Pa; repetition rate of 2 Hz; pulsed fluence of approximately 3.4 J/cm$^2$. As shown in Figure 10a, a $\varphi$-scan was conducted on the (0 1 5) plane of a 200-nm-thick $\text{Bi}_2\text{Te}_3$ film and the (1 1 1) plane of an STO (1 0 0) substrate in skew symmetric geometry by tilting the samples. The in-plane orientation of a hexagonal $h$-$\text{Bi}_2\text{Te}_3$/STO (1 0 0) film displayed a 12-fold symmetry instead of the expected six-
fold symmetry of the (0 1 5) plane in Bi$_2$Te$_3$. Figure 10b shows a schematic drawing of the in-plane atomic arrangement between an h-Bi$_2$Te$_3$ film and an STO (1 0 0) substrate. Since the principal crystallographic orientations of h-Bi$_2$Te$_3$ films grown on STO (1 0 0) substrates can be aligned along either the STO [1 0 0] or STO [0 1 0] directions, the in-plane arrangements result in an observed 12-fold symmetry. The angle differences between STO [0 1 0] and the two orientations of h-Bi$_2$Te$_3$[1 1 0] were 30° and 0°, respectively, as shown in Figure 10b. In other words, the in-plane relationships were Bi$_2$Te$_3$[1 1 0] || STO [0 1 0] and Bi$_2$Te$_3$[1 0 0] || STO [1 0 0]. Lee et al. reported epitaxial growth via domain matching epitaxy of Bi$_2$Se$_3$ thin films on Al$_2$O$_3$(0 0 0 1) substrates with over 13% lattice misfit and a critical thickness of less than one monolayer [64]. A relatively low repetition rate of 0.2 Hz and low $T_S$ of 250°C are key parameters of the PLD growth to achieving high-quality Bi$_2$Se$_3$ epitaxial films. Figure 10c shows $\phi$-scan XRD results performed on [0 1 1 5] planes of the film and [0 1 1 2] planes of the substrate. Clearly, the presence of six peaks corresponding to the Bi$_2$Se$_3$[0 1 1 5] planes confirmed the epitaxy. A schematic depicting twin/domain growth and direction in the study is illustrated in Figure 10d [64]. In one case, the Bi$_2$Se$_3$ basal plane is aligned with that of Al$_2$O$_3$, and in the other, there is a rotation of 60°/180°. The epitaxial relationships are written as (0 0 0 1) Bi$_2$Se$_3$ || (0 0 0 1) Al$_2$O$_3$ or [2 1 0 1] Bi$_2$Se$_3$ || [1 1 2 0] Al$_2$O$_3$. Figure 10e shows the typical $\phi$-scan patterns of hexagonal h-Bi$_3$Se$_2$Te/h-Al$_2$O$_3$ (0 0 0 1) [9]. With the skew symmetric geometry, the $\phi$-scan measurements were performed on the (1 1 6) plane of Al$_2$O$_3$ substrates and the (1 1 12) plane of Bi$_3$Se$_2$Te films. As shown in Figure 10e, the in-plane orientations of both Al$_2$O$_3$ (1 1 6) and Bi$_3$Se$_2$Te (1 1 12) exhibited six-fold symmetries with a 30° difference. Figure 10f illustrates the in-plane atomic arrangement between h-Bi$_3$Se$_2$Te and h-Al$_2$O$_3$ (0 0 0 1). The epitaxial relationship between the films and substrates is (0 0 0 1) Bi$_3$Se$_2$Te || (0 0 0 1) Al$_2$O$_3$ or [2 1 0 1] Al$_2$O$_3$. This in-plane orientation was established to obtain the optimal lattice matching.

5.2. Magnetotransport properties of bismuth chalcogenide thin films

The weak antilocalization (WAL) which is a negative quantum correction to classical MR caused by the wave nature of electrons is used as a signature of TSS. In TIs, WAL is induced by both the helicity of the surface state and the spin-orbit coupling of bulk [4, 61, 65, 66]. In a low $B$ field, the 2D WAL MR of a system with strong spin-orbit interaction can be described using the Hikami-Larkin-Nagaoka model [65], which is [4, 60, 61]

$$\frac{\Delta R_W(B)}{R_W(0)} = -\alpha \frac{e^2}{2\pi^2\hbar} \left[ \Psi \left( \frac{1}{2} + \frac{B_\phi}{B} \right) - \ln \left( \frac{B_\phi}{B} \right) \right]$$

(8)

where $R_W$ is the sheet resistance, $\Delta R_W = R_W(B) - R_W(0)$, $\Psi(x)$ is the digamma function, $B_\phi = h/(4e\ell^2_\phi)$ is a magnetic field varying with the coherence length $\ell_\phi$, $\alpha$ is a parameter and reflects the number of conduction channels. In a 3D TI, $\alpha = -1/2$ for a single coherent transport.
channel in the 2D surface states, and $\alpha = -1$ for two independent coherent transport channels with similar $L_\phi$ in the 2D surface states [60, 65].

The typical magnetoresistance (MR) results of some bismuth chalcogenides (i.e., Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_3$Se$_2$Te) thin films grown by PLD are presented in Figure 11 [9, 64, 67]. The Bi$_2$Te$_3$, Bi$_2$Se$_3$,
and Bi$_2$Se$_2$Te thin films were grown on Al$_2$O$_3$ (0 0 0 1) substrates using PLD at $T_s$ of 225, 250, and 250°C, respectively [9, 64, 67]. The WAL effect which presents as a sharp increase in resistance when $B$ increases in the low magnetic field $B$ regime is clearly observed on the films.

Figure 11a, b, e and f show MR curves at several temperatures ($T$) and the extracted $\alpha(T)$ and $L_0(T)$ values using Eq. (8) for the 27-QL (~27 nm)-thick Bi$_2$Te$_3$ and 200-nm-thick Bi$_2$Se$_2$Te thin films [9, 67]. At 2 K, $L_0$ are 158.1 and 195.2 nm, and $L_0$ decreases monotonically with increasing $T$, obeying the power laws, as $L_0$ ~ $T^{-0.30}$ and $L_0$ ~ $T^{-0.79}$ for the Bi$_2$Te$_3$ and Bi$_2$Se$_2$Te films, respectively (Figure 11b and f). Theoretically, the result of $L_0$ ~ $T^{-0.50}$ observed in the 27-QL-thick Bi$_2$Te thin film indicates the predominant electron-electron scattering in 2D weakly disordered systems. The $L_0$ ~ $T^{-0.79}$ is closed to the $L_0$ ~ $T^{-0.75}$ for 3D systems, if e-e scattering is the dominant dephasing source [9]. The electron screening effect in 3D system is more effective than that in 2D systems. However, the e-e scattering is strongly weakened with high carrier densities ($n$ = 10$^{20}$ cm$^{-3}$ for the Bi$_2$Se$_2$Te films [9]). In 3D disordered conductors (namely, in the bulk state), dephasing by electron-phonon (e-ph) scattering would be significant and dominant. The e-ph scattering also causes a faster decay rate on $L_0$ that is, $L_0$ ~ $T^{-1.0}$ [68]. Additionally, the combination of 2D e-e scattering in the TSS thin layer and e-ph scattering in the bulk would further result in the $L_0$ ~ $T^{-0.79}$. Consequently, e-ph scattering could be the force of channel separation as temperatures increase. It is worthy of mentioning that the MR result is a signature (not conclusive evidence) for the presence of TSS on Bi$_2$Se$_2$Te films. Further theoretical calculations and experiments are needed for reaching a final conclusion.

Figure 11b and f also present the $-\alpha(T)$ results of the Bi$_2$Te$_3$ and Bi$_2$Se$_2$Te films. The $-\alpha$ values of the Bi$_2$Te$_3$ film increase with increasing $T$ from 0.43 at 2 K to 0.45 at 10 K, indicating the existence of a single coherent transport channel (i.e., likely a single surface state) [61]. Meanwhile, the $-\alpha$ values of the 200-nm-thick Bi$_2$Se$_2$Te film increase with increasing $T$ from 0.5 at 2 K to 0.85 at 10 K and to 0.71 at 15 K, suggesting increased channel separation with $T$ [69]. In WAL, the independent phase-coherent channels occur when the carriers in one channel lose phase coherence before being scattered into the other channel.

In Figure 11c, the MR ($B$,$T$) of a 50-nm-thick Bi$_2$Se$_3$ film was measured with $B$ perpendicular to the film plane and ranging from $-9$ T to $+9$ T. At low $B$ and $T$, the distinctive dips of WAL are clearly observed. The WAL effect results from strong spin-orbit coupling, showing the absence of backscattering giving rise to the destructive interference between the two time reversal symmetry loops when there is no magnetic field [64]. Resistance increases sharply with increasing $B$ because the quantum interference is destroyed and backscattering increases (Figure 11c). Figure 11d is the enlarged MR at low $B$ (~2 T to +2 T), and it reveals the existence of WAL as a function of $T$ in a discernible way [64]. WAL gradually weakens as temperature increases, eventually disappearing entirely at $T = 48$ K; thus, the dependence on $B$ is quadratic-like at low field. The MR cusp feature at low $B$ is broadened and finally disappears with increasing temperature owing to the decrease in the phase coherence length. In addition to the WAL effect, Figure 11c shows a 2D, non-saturating linear MR at high $B$, which usually occurs with several TI materials of Bi$_2$Se$_3$ [70], Bi$_2$Te$_3$ [71], Bi$_2$Te$_2$Se [72], and Bi$_2$Se$_2$Te [9]. Theoretical models propose that the linear MR can appear in the gapless linear-dispersive energy spectrum when only the first band level is filled [73, 74], or in the presence of both the gapless linear
spectrum and Landau level overlaps [75]. Noticeably, the WAL and linear MR simultaneously reflect the 3D contribution of spin-orbit coupling in bulk and the Dirac nature of the 2D surface states. Because the magneto transport is a bulk sensitive measurement, it remains a major challenge to directly probe the topological nature [64].

5.3. Proximity-induced superconductivities in Bi inclusions/bismuth chalcogenide thin films

Recent studies have shown a two-dimensional interface state between TIs and superconductors resulting from the superconducting proximity effect that supports Majorana fermions [76, 77]. Majorana fermions, novel particles which are their own antiparticles, can potentially be applied to topological quantum computing, which has motivated intense interest in TIs [53].

Figure 12. (a) Temperature-dependent normalized $ab$ resistivities ($\rho/\rho_{300\,K}$) between 1.8 and 300 K of 46- and 200-nm-thick Bi$_2$Te$_3$ films. Upper inset: an EDS mapping image of a typical Bi-rich cluster. Lower inset: zoomed-in view of the $\rho/\rho_{300\,K}$ in the low temperature range. (b) $\rho(T)$ in 1.75–6.0 K of the 200 nm film at various $H_{||c}$ from 0 to 1 T. Inset: the onset $T_c$ of the two superconducting transitions as a function of magnetic field. (c) Auger electron spectroscopy (AES) elemental depth profiling of a non-superconducting (46-nm-thick) and a superconducting (200-nm-thick) Bi$_2$Te$_3$ films. (d and e) The size distribution of Bi-rich clusters and Bi nanoclusters inside the clusters. (f) Schematics of the surface characteristics and a suggested superconducting mechanism in the Bi$_2$Te$_3$ films [53].
Koren et al. observed the local superconductivity in Bi\textsubscript{2}Te\textsubscript{2}Se and Bi\textsubscript{2}Se\textsubscript{3} films below 2–3 K, which was naturally induced by small amounts of superconducting Bi inclusions or precipitations on the surface [78]. Moreover, Le et al. reported superconductivity at an onset critical temperature of approximately 3.1 K in a topological insulator 200-nm-thick Bi\textsubscript{2}Te\textsubscript{3} thin film grown by pulsed laser deposition [53]. Indeed, Figure 12a shows the normalized resistivity \(\rho/\rho_{300\,\text{K}}\) of a 46-nm-thick Bi\textsubscript{2}Te\textsubscript{3} film (S\textsubscript{1}) and a 200-nm-thick Bi\textsubscript{2}Te\textsubscript{3} film (S\textsubscript{2}) as functions of temperatures (\(T\)) from 1.8 to 300 K. Both films show a decrease in resistivity (\(\rho\)) with decreasing \(T\) in the range of 20–300 K, implying that the films exhibit weak metallic properties commonly seen in narrow band-gap semiconductors with high carrier concentrations [53]. Below 20 K (Figure 12a, the lower inset), the \(\rho/\rho_{300\,\text{K}}\) of S\textsubscript{1} shows a gentle upturn because of the weak localization of electrons [7], whereas the \(\rho/\rho_{300\,\text{K}}\) of S\textsubscript{2} reaches a plateau before dropping sharply at \(T_{c1} = 5.8\) K and then sharply at \(T_{c2} = 3.1\) K. Figure 12b further shows the \(H_{||c}\)-dependent \(\rho(T)\) of S\textsubscript{2} in the low \(T\) regime, where \(H_{||c}\) is the applied magnetic field along the \(c\)-axis of the film. At \(H_{||c} = 0\), \(\rho\) drops abruptly by 8% below \(T_{c2}^{\text{onset}}\) but does not go down to zero, even at \(T = 1.8\) K. This nonzero \(\rho\) at low \(T\) indicates that the superconducting volume ratio is not 100%.

The inset in Figure 12b shows that the \(T_{c2}^{\text{onset}}(\rho_{c2}^{\text{onset}})\) decreases from 3.1 (5.8) to 1.8 (5.4) K with increasing \(H_{||c}\) from 0 to 0.2 T, strongly indicating that both transitions are superconducting in nature.

The detailed investigations of S\textsubscript{2} strongly suggest the existence of superconducting Bi nano-clusters on the surface that induce the \(T_{c1} \approx 5.8\) K. EDS lateral elemental mapping revealed that the distributions of Te and Bi were not uniform, and many Bi-rich (47–54 at.%) clusters were visible (green color), as shown in the upper inset in Figure 12a, differing substantially from the uniform distribution and cluster-free surface observed in film S\textsubscript{1}. The size distribution and the most probable size of Bi-rich clusters are in the range of 400–2400 nm and 560–772 nm, respectively. Intriguingly, a closer inspection reveals that Bi-rich clusters are composed by some Bi nanoclusters (or nanograins) with a size of 20–62 nm.

The Bi-rich environment on the film surface is confirmed by AES analysis (Figure 12c) [53]. This is because the vapor pressure of Te (at \(T_{S} = 300\,\text{°C}\)) is approximately 10\textsuperscript{5} times higher than that of Bi, and therefore, more Te atoms are re-evaporated from the 300°C substrates [79]. The loss of Te is more severe in film S\textsubscript{2} than in film S\textsubscript{1}, (14.3% in S\textsubscript{2} and 4.5% in S\textsubscript{1} at depth \(Z = 0\), Figure 12c) because of the six times longer deposition time of S\textsubscript{2} (60 min) compared to S\textsubscript{1} (10 min). In addition, the nonstoichiometric effect is strongly depth-dependent (Figure 12c). The Te/Bi ratio gradually increases toward the stoichiometric ratio of 3/2 in 200-nm-thick films or slightly exceeds it (Te-rich) in 46-nm-thick films when the depth (\(Z\)) of the films increases. Under such a sufficiently high surface concentration of Bi atoms, the Bi clusters precipitate and segregate readily on the surface to minimize overall free energy, as long as the substrate temperature of 300°C is higher than the 271°C melting point of Bi, as demonstrated in Figure 12f. Notably, the Bi clusters can only be observed in highly Bi-rich (14.3% at \(Z = 0\)) films (S\textsubscript{2}) and not in low Bi-rich (4.5% at \(Z = 0\)) films (S\textsubscript{1}), suggesting a critical Bi-rich concentration for Bi precipitation (separating a Bi phase) in a Bi\textsubscript{2}Te\textsubscript{3} film [53]. The \(T_{c1}\) at ~5.8 K found in our samples should be induced by the superconducting transition of the Bi nanoclusters, which is
closely consistent with the $T_c$ of 6.3 K for the surface Bi islands observed in Bi$_2$Te$_3$Se films [78]. The tiny resistivity drop at $T_{c1} = 5.8$ K (by approximately 0.5%, Figure 12b) indicates that the amount of superconducting Bi nanoclusters in S$_2$ is likely small and, therefore, the Josephson coupling between these islands is extremely weak. Since the superconductivity of Bi nanoclusters survived until $H_{c1} = 1.0$ T (Figure 12b), the critical field of Bi nanoclusters is in between 0.3 and 1.0 T. This section demonstrates that natural defects generated during PLD growths, namely superconducting Bi nanoclusters or Bi inclusions, can substantially induce non-superconducting TI thin films (i.e., Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_2$Te$_2$Se) into superconducting states at low temperatures.

6. Conclusion

This chapter provides the effects of ambient pressures and substrate temperatures in PLD growths on the structural-morphology, thermoelectric, nanomechanical, and magnetoresistance properties of bismuth chalcogenide thin films. The thermoelectric power factor of the stoichiometric Bi$_2$Te$_3$ films grown in the range of 220–340°C and $P_{Ar}$ of 80 Pa reached remarkably high values, ranging between 18.2 ± 0.25 and 24.3 ± 0.44 μW cm$^{-1}$ K$^{-2}$. The optimal PF values were 5.54 ± 0.34 μW cm$^{-1}$ K$^{-2}$ for the layered hexagonal platelet Bi$_2$Se$_3$ films deposited at 300°C and $P_{He}$ of 40 Pa and 8.3 μW cm$^{-1}$ K$^{-2}$ for the nanocrystalline Bi$_2$Se$_3$Te films deposited at 250°C and $P_{He}$ of 40 Pa. We also reported the effects of $P_{He}$ in PLD on nanomechanical properties (i.e., hardness and Young’s modulus) of Bi$_2$Te$_3$ and Bi$_2$Se$_3$Te thin films. It was observed that the hardness and Young’s modulus increased with increasing $P_{He}$, depending on the grain sizes following the inverse Hall-Petch effect for Bi$_2$Te$_3$ films grown at $P_{He}$ $\leq$ 2.0 $\times$ 10$^{-3}$ Torr and following the Hall-Petch relationship for Bi$_2$Se$_3$Te grown at $P_{He}$ of 2.0 $\times$ 10$^{-5}$ to 6.5 $\times$ 10$^{-1}$ Torr. PLD has been successfully employed to grow epitaxially bismuth chalcogenide thin films on large-misfit substrates, for example, Bi$_2$Te$_3$/SrTiO$_3$ (1 0 0), Bi$_2$Se$_3$/Al$_2$O$_3$ (0 0 0 1), and Bi$_2$Se$_3$Te/Al$_2$O$_3$ (0 0 0 1). The magnetotransport studies show that the bismuth chalcogenide thin films such as Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Bi$_2$Se$_3$Te films present a two-dimensional weak antilocalization effect in a low magnetic field ($B$) regime and linear magnetoresistance in a high $B$ regime, which could be attributed to the topological insulator surface states. Furthermore, proximity-induced superconductivities in Bi$_2$Te$_3$ thin films have an onset $T_c$ of approximately 3.1 K, evidently induced by Bi inclusions (nanoclusters with onset $T_c$ at 5.8 K) segregated on the surface of films.

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