A comprehensive review on Bi$_2$Te$_3$-based thin films: Thermoelectrics and beyond

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Abstract
Bi$_2$Te$_3$-based materials are not only the most important and widely used room temperature thermoelectric (TE) materials but are also canonical examples of topological insulators in which the topological surface states are protected by the time-reversal symmetry. High-performance thin films based on Bi$_2$Te$_3$ have attracted worldwide attention during the past two decades due primarily to their outstanding TE performance as highly efficient TE coolers and as miniature and flexible TE power generators for a variety of electronic devices. Moreover, intriguing topological phenomena, such as the quantum anomalous Hall effect and topological superconductivity discovered in Bi$_2$Te$_3$-based thin films and heterostructures, have shaped research directions in the field of condensed matter physics. In Bi$_2$Te$_3$-based films and heterostructures, delicate control of the carrier transport, film composition, and microstructure are prerequisites for successful device operations as well as for experimental verification of exotic topological phenomena. This review summarizes the recent progress made in atomic defect engineering, carrier tuning, and band engineering down to a nanoscale regime and how it relates to the growth and fabrication of high-quality Bi$_2$Te$_3$-based films. The review also briefly discusses the physical insight into the exciting field of topological phenomena that were so dramatically realized in Bi$_2$Te$_3$- and Bi$_2$Se$_3$-based structures. It is expected that Bi$_2$Te$_3$-based thin films and heterostructures will play an ever more prominent role as flexible TE devices collecting and converting low-level (body) heat into electricity for numerous electronic applications. It is also likely that such films will continue to be a remarkable platform for the realization of novel topological phenomena.

KEYWORDS
Bi$_2$Te$_3$-based thin films and heterostructures, device applications, thermoelectric, topological phenomena

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1 | INTRODUCTION

In the past few years, emerging industrial fields, such as 5G communications, “Internet of Things” network, and wearable electronics have demonstrated a great demand for miniaturized refrigeration and power generation based on high-performance room temperature thermoelectric (TE) materials.[1–8] The key parameter, “the dimensionless thermoelectric figure-of-merit $ZT$,” defined as $ZT = S^2\sigma T/\kappa$ is a measure of the conversion efficiency of a TE device. Here, $S$, $\sigma$, $T$ are Seebeck coefficient, electrical conductivity, and absolute temperature, respectively. The parameter $\kappa$ stands for the total thermal conductivity that is comprised of the lattice thermal conductivity $\kappa_L$, the electronic thermal conductivity $\kappa_e$, and the so-called bipolar thermal conductivity $\kappa_b$.[9,10]

Apart from a low thermal conductivity, a successful TE device operation requires that the TE power factor ($PF = S^2\sigma$) is large. Even today, some 70 years since Goldsmid discovered Bi$_2$Te$_3$ as a very promising TE,[11] the Bi$_2$Te$_3$-based materials are the most efficient and most extensively studied room temperature TE materials, and in their bulk form dominate commercial TE applications.[5,12] Figure 1B summarizes the reported $ZT_{\text{max}}$ values for both p- and n-type Bi$_2$Te$_3$-based bulk structures. By optimizing the composition and microstructure, the $ZT$ values of both p- and n-type Bi$_2$Te$_3$-based bulk materials have been steadily improved, and currently reach values of 1.3–1.8 and 1.0–1.4, respectively. Such high-performance bulk materials have established the benchmark for efficient device operations as TE coolers and TE power generators. Equally important, the thin film forms of Bi$_2$Te$_3$-based materials have also attracted tremendous attention from researchers and engineers working in the field of thermoelectricity. Thin films of Bi$_2$Te$_3$-based structures are very attractive and suitable for emerging applications in flexible and miniaturized electronic devices.[1,3,8]

The high TE performance of Bi$_2$Te$_3$-based materials derives from their characteristic crystal lattice and from

![Figure 1](image-url)

**Figure 1** Thermoelectric effects and basic physical properties of Bi$_2$Te$_3$-based compounds. (A) The Seebeck effect (left) and the Peltier effect (right). (B) The summary of reported $ZT_{\text{max}}$ in both n-[12–26] and p-type[27–46] Bi$_2$Te$_3$-based bulk materials. (C) Crystal structure of the rhombohedral-phase Bi$_2$Te$_3$. (D) Band structure of bulk Bi$_2$Te$_3$ calculated with the LDA functional. Red and blue curves indicate calculations with and without spin orbit coupling (SOC). Reproduced from Ref. [47] (E) Depiction of the effect of SOC on the band structure of Bi$_2$Te$_3$. Reproduced from Ref. [48] Copyright 2019, John Wiley and Sons. SOC causes the gap closing and band inversion and induces a new gap and topological surface states (TSS) in the gap. (F) Schematic diagram of crystal structures of Cr-doped (Bi,Sb)$_2$Te$_3$ and MnBi$_2$Te$_4$. (G) A sketch of the gapped Dirac-like dispersion of surface states (left) and the dissipationless chiral edge transport (right) in a magnetic topological insulator. Reproduced from Ref. [49] Copyright 2019, Springer Nature
their favorable electronic band structure, as illustrated in Figure 1C–E and Table 1. The Bi₂Te₃-based compounds, collectively known as tetradymite-type structures, include Bi₂Te₃, Sb₂Te₃, and Bi₂Se₃, all of which crystallize in a rhombohedral structure with the space group R-3m, as shown in Figure 1C.⁵⁰,⁵¹ Taking Bi₂Te₃ as an example, the quintuple layers (QLs) of Te(1)–Bi–Te(2)–Bi–Te(1) are stacked in a sequence along the crystallographic c-axis direction in which there are two inequivalent Te lattice sites, Te(1) and Te(2). Te–Bi bonds are of a substantially covalent nature, while the bonding between adjacent QLs is formed by weak van der Waals (vdW) bonds. The layered structure of Bi₂Te₃, including the weak Te(1) bonds, leads to anisotropic electrical and thermal transport properties.⁵²,⁵³ Because the carrier scattering along the c-axis (⊥) is markedly stronger than in the plane of the layers (∥), the in-plane electrical conductivity σ∥ is much larger than the perpendicular conductivity σ⊥. Typical anisotropies σ∥/σ⊥ are in the range of 3–7 in n-type Bi₂Te₃ and in the range of 2–4 in p-type Bi₂Te₃. Corresponding anisotropies in the thermal conductivity κ∥/κ⊥ are of about 2–2.5 for both n-type and p-type Bi₂Te₃.⁵⁴–⁵⁶ Hence, correlations between the crystal orientation and TE properties are important in all forms of Bi₂Te₃-based materials.

The spin-orbit coupling (SOC) plays a vital role in the formation of a band gap, valley degeneracy, and non-trivial band topology of Bi₂Te₃-based materials, as shown in Figure 1D,E. In the absence of SOC, theoretical calculations have predicted that Bi₂Te₃ has a direct band gap at the Γ point in the Brillouin zone, and that the conduction band minimum (CBM) and the valence band maximum (VBM) are primarily composed of Bi 6p and Te 5p orbitals, respectively.⁴⁷,⁴⁸,⁶⁷,⁶⁸ Due to the different strengths of SOC in Bi and Te, the presence of SOC reduces the energy of the Bi 6p orbital more than that of the Te 5p orbitals. Consequently, the CBM shifts down and crosses the VBM, causing a band inversion. The strong SOC in Bi₂Te₃ further results in an anticrossing of the inverted bands and a new gap opens near the Γ point. On one hand, this band evolution leads to almost linearly dispersing bands that possess small band effective mass (m*ₐ) and high band degeneracy (Nᵥₑ) as the band edges have shifted slightly away from the high symmetry Γ point. The high band degeneracy is particularly beneficial for achieving a large PF = S²σ that is proportional to (Nᵥₑ)²/₃(m*ₐ)⁴/₃μ.⁴⁸,⁶⁸ For example, Bi₂Te₃ and Sb₂Te₃ have a high Nᵥₑ = 6 near CBM and VBM as well as a high carrier mobility μ. On the other hand, the band inversion and the strong SOC induce topologically protected surface states (TSS) and a massless Dirac point (DP), leading to the gapped Bi₂Te₃-based materials becoming the well-known three-dimensional (3D) topological insulators (TIs).⁶⁹,⁷⁰ The TSS have their spin locked with their momentum and are protected by time-reversal symmetry, which is immune to structural disorders but sensitive to magnetic perturbations. Introducing magnetism in the Bi₂Te₃-based TIs by doping with magnetic species, such as Cr,⁷¹,⁷² V,⁷³,⁷⁴ and Fe⁷⁵ or by intercalating magnetic bilayers of MnTe,⁷⁶,⁷⁷ the exotic quantum anomalous Hall (QAH) effect can be realized, as shown in Figure 1F,G. In such QAH insulators, the ferromagnetic order gives rise to a band gap opening at the DP and a dissipationless edge transport channel that is topologically protected.

To provide a comprehensive understanding of Bi₂Te₃-based thin films, the review will discuss the role of microstructure in relation to the TE properties and how it provides a regulation mechanism for transport in both n- and p-type forms of Bi₂Te₃-based films. Unless specifically mentioned in the following sections, we focus on transport data that are obtained by in-plane measurements. Device performance will be discussed mostly in the context of miniaturized and flexible n- and p-type Bi₂Te₃-based films. Finally, the intriguing topological phenomena related to Bi₂Te₃-based TIs and magnetic TIs are briefly commented upon, including the QAH effect, the SOC proximity effect, and the superconducting proximity effect, all discovered in the 2D form of the structure.

### Table 1 Basic physical properties of Bi₂Te₃, Sb₂Te₃, and Bi₂Se₃

| Material | Type | Eᵥ (eV) | Nᵥ | m*ᵥ (L) | m*ᵥ (∥) | κᵥ (L) (Wm⁻¹K⁻¹) | κᵥ (∥) (Wm⁻¹K⁻¹) | Ref. |
|----------|------|--------|----|----------|----------|------------------|------------------|-----|
| Bi₂Te₃   | n    | 0.14   | 6  | 0.22     | 0.08     | 1.43             | 2.42             | [57–60] |
| Bi₂Te₃   | p    | 0.14   | 6  | 0.28     | 0.11     | 1.43             | 2.42             | [57,58,60,61] |
| Bi₂Se₃   | n    | 0.3    | 1  | 0.58     | 0.15     | 0.48             | 1.58             | [62–64] |
| Sb₂Te₃   | p    | 0.24   | 6  | 0.29     | 0.11     | 1.9              | 5                | [61,65,66] |

Abbreviations: Eᵥ, band gap; Nᵥ, band degeneracy; m*ᵥ, single valley effective mass; κᵥ, lattice thermal conductivity; L, in-plane; ∥, cross plane.
FABRICATION AND TE PROPERTIES OF Bi₂Te₃-BASED FILMS

As proposed by Dresselhaus and coworkers in the early 1990s, lower-dimensional structures, such as thin films, superlattices (SLs), and heterostructures, hold a great promise for enhancing the TE performance because of strong quantum confinement and strengthened boundary scattering associated with the presence of numerous interfaces.\[^{78-80}\] The proposal generated much interest and provided a strong impetus for explorations of Bi₂Te₃-based thin films and SLs. Currently, various techniques are being utilized for the fabrication of Bi₂Te₃-based thin films, among them are metal-organic chemical vapor deposition (CVD),\[^{81-83}\] electrochemical deposition (ECD),\[^{84,85}\] molecular beam epitaxy (MBE),\[^{86-88}\] thermal coevaporation,\[^{89-91}\] magnetron sputtering (MS),\[^{92-95}\] and pulsed laser deposition (PLD).\[^{96-98}\]

The film growth is a nonequilibrium kinetic process in which the rate-limiting steps strongly affect the growth mode, morphology, microstructure, and composition of the grown films.\[^{99}\] Delicate control of the film growth parameters is of crucial importance for manipulating the crystallinity, orientation, and atomic defects and hence the overall TE performance of Bi₂Te₃-based thin films. Moreover, a firm command of the film growth and the quality of the resulting films is a prerequisite to achieving an excellent TE performance and carrying out a successful exploration of intriguing physical phenomena realized in Bi₂Te₃-based films.

2.1 Growth mechanism of Bi₂Te₃-based films

Figure 2 schematically illustrates three predominant preferential orientations observed in the fabricated Bi₂Te₃-based thin films and the corresponding microstructures and formation mechanisms. Generally, under stable growth conditions, Bi₂Te₃-based thin films are featured by the layer-by-layer growth mode and the (00l) oriented structure regardless of the choice of substrates or deposition techniques.\[^{88,91,97,98,100,101}\] This has its origin in the weak vdW interactions between the adjacent QLs. In contrast, Bi₂Te₃-based thin films with crystalline orientations other than (00l) or even amorphous structures can be fabricated under unstable conditions.

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**FIGURE 2** Three predominant preferential orientations and the corresponding growth mechanism of Bi₂Te₃-based films. Bottom panel: the (00l)-oriented structure of sequentially stacked Bi₂Te₃ QLs revealed by TEM and the surface morphology observed by AFM. Middle panel: The (015)-oriented structure showing lamellas tilted by a certain angle from the substrate surface. The formation of Bi₂Te₃ with this preferred orientation is explained by differences in the atomic density and the surface free energy of crystal planes. Reproduced from Ref. [104] Copyright 2019, John Wiley and Sons. Upper panel: the (110)-oriented structure with lamellas standing perpendicular to the substrate surface. The high stacking density, the external electric field, and the directional solidification are extra driving forces for the formation of the (110)-oriented structure. Reproduced from Ref. [103] Copyright 2015, Royal Society of Chemistry. AFM, atomic force microscopy; QL, quintuple layer; TEM, transmission electron microscopy.
growth conditions. Herein, the crystalline orientation will be elucidated from the growth kinetics of thin films. The film growth process is mainly determined by the substrate temperature \(T_{\text{sub}}\) and the elementary fluxes supplied by the evaporation sources. In turn, the above growth conditions affect the nucleation rate, the growth rate, and the microstructure of the grown films. First, under a suitable \(T_{\text{sub}}\) and a low growth rate, Bi\(_2\)Te\(_3\)-based thin films can be grown stably by the process of layer-by-layer growth and their microstructure is typified by the (00l) orientation. As documented by the MBE-grown films grown under stable conditions, for example, under a rather low \(T_{\text{sub}}\) and at too high growth rates, see the middle panel in Figure 2. This is mainly ascribed to the lowest surface free energy and the highest atomic density in this plane as compared to similar crystalline planes of (0 3 5), (0 1 11), and (0 1 1). Commonly, a minor (1 1 0) X-ray diffraction peak may also appear in the films with the dominant (0 1 5) crystalline orientation, indicating random stacking of the crystal grains. Third, the Bi\(_2\)Te\(_3\)-based thin films can also be fabricated with the (1 1 0) preferential orientation, which, however, is energetically unfavorable compared to the aforementioned film orientations. As depicted in the top panel of Figure 2, extra driving forces are required for this particular film orientation, which may include a very high stacking density of elementary fluxes during the MS deposition process and the presence of external electrical fields in the ECD process, and the directional solidification during the selective laser melting process. On the whole, the CVD process and physical vapor depositions (including MBE, PLD, and MS) are able to grow high quality and (00l)-oriented Bi\(_2\)Te\(_3\)-based thin films, provided the films are grown under stable conditions, as listed in Table 2. It is worth noting that the (00l) and (015) crystalline orientations in Bi\(_2\)Te\(_3\)-based thin films can be enhanced by postannealing treatments at elevated temperatures. This is due to the significantly enhanced migration of the constituent atoms and recrystallization of the grains. The resulting crystalline orientation is highly relevant for the optimization of the TE performance of Bi\(_2\)Te\(_3\)-based thin films and is also an important factor during the integration and application of thin film structures in TE devices.

### 2.2 Overall TE transport features of Bi\(_2\)Te\(_3\)-based films

N-type Bi\(_2\)Te\(_3\) films and p-type Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) films with their (00l)-oriented structure are the most widely explored structures due to their excellent \(n_\text{eff}\), \(\mu\), and \(PF\), as shown in Table 2. In various studies, strategies based on atomic defect engineering and the control of crystalline orientation and microstructure have proved to be very effective for optimizing the electronic properties of Bi\(_2\)Te\(_3\)-based thin films. Nevertheless, the literature data on the electronic transport properties vary drastically even when the carrier concentrations are comparable. This indicates that it is very challenging to tune effectively the electronic properties in Bi\(_2\)Te\(_3\)-based thin films, similar to the drastic variations in the electronic properties found in their bulk counterparts. So far, three important aspects regarding the transport properties could be identified in Bi\(_2\)Te\(_3\)-based thin films.

1. Atomic defect engineering: defect formation energy calculations and advanced experimental characterizations have revealed that vacancies at the anion sites (V\(_{\text{Se}}\) and V\(_{\text{Te}}\)) and anti-site defects at both anion and cation sites (Bi\(_{\text{Te}}\), S\(_{\text{Bi}}\), and Te\(_{\text{Bi}}\)) have the lowest formation energies and thus are the dominant atomic defects in thin Bi\(_2\)Te\(_3\)-based films. The manipulation of atomic defects and their density is crucial for the optimization of the \(PF\) of the films, as will be clarified in Sections 3 and 4.

2. Optimal PFs in n-type and p-type films: n-type single crystalline Bi\(_2\)Te\(_3\) films with optimized atomic defects and the electron density \(n_\text{e}\approx 10 \times 10^{19} \text{cm}^{-3}\) attain the best room temperature \(PFs\) of about 5.0 mWm\(^{-1}\)K\(^{-2}\), equal to the value obtained in bulk single crystals. The overall \(PFs\) of p-type films with compositions close to Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) are superior to that of n-type Bi\(_2\)Te\(_3\) films, revealing that the atomic defect engineering is more challenging in the n-type form of the film structure. Under the optimal hole density \(n_\text{p}\), and with (00l) and (015) preferential orientations, n-type films reach \(PFs\) better than 3.5 mWm\(^{-1}\)K\(^{-2}\). The “3ω” method and the time-domain thermoreflectance method are two methods, which have been used to measure the thermal conductivity of thin films but the specialized apparatus they require is rather uncommon in most labs. Nevertheless, the existing data sets indicate that the thermal conductivity of Bi\(_2\)Te\(_3\)-based thin films is very close to the values reported for bulk single crystals, which suggests that the ZTs in the films are unlikely to exceed ZT values in bulk samples.
| Year | Method | Substrate | Film | n  | μ   | σ  | |         |         |         |   |   |   | S  |       |       |
|------|--------|-----------|------|----|----|----|---|--------|--------|
| 2009 | PLD    | SiO₂/Si   |      | 10.7 | 90.5 | 11.1 | 183.6 | 5.1    |
| 2011 | MS     | Glass     | (015) | 95.0 | 12.1 | 18.4 | 70.0  | 0.9    |
| 2011 | MBE    | BaF₂ (111) | (000) + (015) | 2.7 | 80.0 | 3.4 | 153.0 | 0.8    |
| 2012 | MS     | SiO₂/Si   | (015) | 5.7 | 50.3 | 100.0 | 4.7  | 0.5    |
| 2012 | MBE    | BaF₂ (111) | (000) | 81.0 | 8.6 | 11.1 | 127.0 | 1.8    |
| 2013 | CE     | Glass     | (015) | 37.3 | 10.2 | 6.7 | 160.0 | 1.6    |
| 2013 | MS     | Glass     | (0111) | 5.5 | 99.0 | 3.6 | 242.0 | 2.1    |
| 2013 | ECD    | Pt/Au-Si  | (015) + (101) | 5.5 | 99.0 | 3.6 | 242.0 | 2.1    |
| 2013 | MS     | SiO₂/Si   | (015) | 3.4 | 99.0 | 3.6 | 242.0 | 2.1    |
| 2013 | MBE    | Al₂O₃(000) | (000) | 5.2 | 75.8 | 5.5 | 212.3 | 2.5    |
| 2016 | MS     | Glass     | (000) | 10.5 | 125.8 | 1.7 | 128.6 | 1.7    |
| 2014 | ECD    | -         | (110) | 6.91 | 146 | 1.5 | 171.5 | 3.5    |
| 2017 | MS     | Glass     | (000) | 6.7 | 113.7 | 11.7 | 171.5 | 3.5    |
| 2017 | MS     | Free-standing | (000) | 5.0 | 65.0 | 5.2 | 172  | 1.6    |
| 2021 | MBE    | Al₂O₃(000) | (000) | 11.1 | 81.0 | 14.4 | 180.0 | 4.7    |

Table 2: Room temperature electronic transport properties of Bi₂Te₃-based films

**n-Type binary Bi₂Te₃-based films**

| Year | Method | Substrate | Film | n  | μ   | σ  | |         |         |         |   |   |   | S  |       |       |
|------|--------|-----------|------|----|----|----|---|--------|--------|
| 2009 | FE     | Glass     |      | 17.8 | 35.1 | 6.2 | 162.9 | 1.7    |
| 2009 | MS     | SiO₂/Si   | (015) | 3.5 | 109.3 | 2.3 | 178  | 1.2    |
| 2007 | FE     | Glass     |      | 5.0 | 65.0 | 5.2 | 172  | 1.6    |
| 2010 | FE     | Glass     | (000) | 24.4 | 72.3 | 27.5 | 97.5  | 2.5    |
| 2013 | PLD    | Si        | (000) | 24.4 | 72.3 | 27.5 | 97.5  | 2.5    |
| 2013 | ECD    | Pt/Au-Si  | (015) + (110) | 6.4 | 237.2 | 3.5 | 237.2 | 3.5    |

**p-Type (Bi,Sb)₂Te₃ films**

(Continues)
| Year  | Method | Substrate | Film | $n$  | $\mu$  | $\sigma$ | $|S|$  | $PF$ |
|-------|--------|-----------|------|------|-------|--------|------|-----|
| 2013  | MS     | AlN       | (001)| 7.5  | 127.7 | 14.6   | 191.3| 5.3 |
| 2014  | IBAD   | SiO$_2$   | (015)| 2.7  | 144   | 6.2    | 249  | 3.8 |
| 2015  | PLD    | Si        | (001)| 14.4 | 51    | 11.8   | 136.9| 2.2 |
| 2015  | MS     | AlN/Pt/Cu | (110) + (015)| –   | –     | 4.5    | 152  | 1.0 |
| 2015  | MS     | SiO$_2$   | (015)| 1.6  | 65.6  | 1.7    | 258.5| 1.1 |
| 2015  | EBV    | Glass     | (015)| 121.5| 15.1  | 113.9  | 36.7 | 1.5 |
| 2016  | PLD    | Glass     | (001) + (110)| 3.9 | 141   | 11.8   | 169  | 3.3 |
| 2020  | FE     | Flexible polyimide | (001)| 0.7  | 375   | 4.2    | 270  | 3.1 |
| 2020  | MS     | Al$_2$O$_3$ | (001)| 22.7 | 32.4  | 16.1   | 133.2| 2.9 |

p-Type 1 nm Bi$_2$Te$_3$/5 nm Sb$_2$Te$_3$ superlattices

| Year  | Method | Substrate | Film | $n$  | $\mu$  | $\sigma$ | $|S|$  | $PF$ |
|-------|--------|-----------|------|------|-------|--------|------|-----|
| 2001  | CVD    | GaAs(001) | (001)| 3.0  | 383   | ~19.0  | 200–270| –   |
| 2016  | CVD    | GaAs(001) | (001)| –    | –     | 10.0   | 238  | 5.7 |

Note: The in-plane carrier density, $n$ ($10^{19}$ cm$^{-3}$); carrier mobility, $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$); electrical conductivity, $\sigma$ (10$^4$ Sm$^{-1}$); Seebeck coefficient, $S$ ($\mu$V K$^{-1}$); power factor, $PF = S^2 \sigma$ (mW m$^{-1}$ K$^{-2}$). The respective properties for 1 nm Bi$_2$Te$_3$/5 nm Sb$_2$Te$_3$ superlattices reported in 2001 were determined in the cross-plane direction, that is, perpendicular to the film plane.

Abbreviations: CVD, chemical vapor deposition; EBV, e-beam evaporation; ECD, electrochemical deposition; FE, flash evaporation; IBAD, ion beam assisted deposition; MBE, molecular beam epitaxy; MS, magnetron sputtering; PLD, pulsed laser deposition.
The study of Bi$_2$Te$_3$-based SLs has always been an important topic in the TE community. In 2001, Venkatasubramanian et al.\cite{82} reported on the CVD fabrication of p-type Bi$_2$Te$_3$/Sb$_2$Te$_3$ SLs and on a record high ZT of 2.4 at 300 K, which inspires a widespread research interest to search for high ZTs in structures with reduced dimensionality. Unfortunately, this spectacular success was not reproduced in spite of intense experimental efforts globally.\cite{129} Hansen et al.,\cite{130} have successfully reproduced the 1 nm Bi$_2$Te$_3$/5 nm Sb$_2$Te$_3$ SL by the MBE growth; however, the obtained in-plane electronic properties were significantly inferior to the values reported by Venkatasubramanian et al.\cite{82} Meanwhile, Bulman et al.\cite{83} reported on the TE properties of the similar SL but, again, the in-plane PF was smaller than that reported by Venkatasubramanian et al.,\cite{82} leading to a significantly lower ZT of 1.4 at 300 K. Thus, growing SLs as a means of enhancing ZT values remains controversial and under debate.

3 | STRATEGIES ON OPTIMIZING THE ELECTRONIC PROPERTIES OF N-TYPE Bi$_2$Te$_3$-BASED FILMS

Similar to the adopted strategies in the case of bulk n-type Bi$_2$Te$_3$-based materials,\cite{131-136} atomic defect engineering, typified by explorations of the interfacial effect and the preferential orientation, also play an important role in tuning the electronic transport properties of n-type Bi$_2$Te$_3$-based films. It should be pointed out that most of the studies on n-type films are based on binary Bi$_2$Te$_3$. Because the thin films deposition processes are very different from the bulk synthesis routes, the tuning mechanisms of atomic defects and the interfacial effect in Bi$_2$Te$_3$ films differ significantly from that in bulk Bi$_2$Te$_3$ structures. Moreover, the advanced tools of scanning tunneling microscopy and angle-resolved photoemission spectroscopy (ARPES) have recently been added as powerful tools to study directly the influence of atomic defects on the electronic transport properties of n-type Bi$_2$Te$_3$ films.\cite{101,105,111} The comprehensive analysis has unambiguously revealed that the carrier density $n_e$, the carrier mobility $\mu$, the effective mass $m^*$, and PF of n-type Bi$_2$Te$_3$ films could be conveniently tailored through the manipulation of atomic defects.

3.1 | Atomic defect engineering

Among the various thin film growth parameters, the $T_{\text{sub}}$, and the postannealing processing could remarkably alter the formation and transformation of atomic defects and thus the electronic transport properties of n-type Bi$_2$Te$_3$ films. Our results\cite{101} and the studies from other laboratories\cite{81,92,132,133} have shown that the substrate temperatures $T_{\text{sub}}$ in the range of 240–350°C are suitable for the stable growth of high-quality Bi$_2$Te$_3$ films. Because the thermal evaporation temperature of Te is around 220°C, which is obviously lower than the optimal $T_{\text{sub}}$, Bi$_2$Te$_3$ films are generally grown under a Te-poor environment due to a serious re-evaporation of Te from the heated substrate. Moreover, because the elemental Bi is evaporated at temperatures above 500°C, the efficient migration of Bi atoms is unlikely to take place on the heated substrate with $T_{\text{sub}}$ much lower than its evaporation temperature. The above two aspects indicate that the reaction-driven formation of n-type Te vacancies V$_{\text{Te}}$ can easily happen in Bi$_2$Te$_3$ films. The presence of V$_{\text{Te}}$ vacancies answers the long-standing puzzle of why nominally undoped Bi$_2$Te$_3$ films have always shown n-type conduction.\cite{52,100,113}

As summarized in Figure 3A, the carrier concentration $n_e$ of n-type Bi$_2$Te$_3$ films tends to increase with the increasing $T_{\text{sub}}$. This upward trend in $n_e$ could be explained by progressively more intense re-evaporation of Te and the generation of a greater density of V$_{\text{Te}}$ vacancies. Moreover, the elevated substrate temperature $T_{\text{sub}}$ will lead to transformations of n-type vacancies V$_{\text{Te}}$ to p-type antisite defects Bi$_{\text{Te}}$ that possess the lowest formation energy among all defects generated when the growth proceeds under the condition of Te deficiency.\cite{101,105,119}

The resulting nonmonotonic increase in the carrier concentration $n_e$ with the increasing $T_{\text{sub}}$ is due to the fact that $T_{\text{sub}}$ affects the density of both n-type V$_{\text{Te}}$ and p-type Bi$_{\text{Te}}$. As documented by the values of PFs from different groups, see Figure 3B, it is obvious that the optimized PFs in Bi$_2$Te$_3$ films are in the range of 2.5–3.5 mWm$^{-1}$K$^{-2}$ at $T_{\text{sub}} = 240–300°C$. Measurements made by Lee et al.\cite{81} and Zhang et al.\cite{101} on single crystalline Bi$_2$Te$_3$ films with the optimal carrier concentration of $7\times9\times10^{19}$ cm$^{-3}$ attained the highest PF of $\sim 3.5$ mWm$^{-1}$K$^{-2}$. Similar to the effect of $T_{\text{sub}}$, the annealing temperature ($T_{\text{ann}}$) and the annealing time ($t_{\text{ann}}$) during the postannealing process can also regulate atomic defects in Bi$_2$Te$_3$ films. Wang et al.\cite{165} have revealed that in Bi$_2$Te$_3$ films, the annealing promotes the (00l)-orientation and the growth of crystal grains, resulting in an enhancement of the carrier mobility $\mu$ from 8 to 98.6 cm$^2$V$^{-1}$s$^{-1}$ and the PF boosted by 300%. As depicted in Figure 3C–F, the carrier density $n_e$ of Bi$_2$Te$_3$ films shows a decreasing trend with the increasing $T_{\text{ann}}$ and $t_{\text{ann}}$, while there is no clear trend in the PFs in postannealed Bi$_2$Te$_3$ films. This is likely a result of V$_{\text{Te}}$ transforming to Bi$_{\text{Te}}$ during the postannealing process and the consequent change in the density of V$_{\text{Te}}$ and Bi$_{\text{Te}}$. Although the carrier concentration is within the optimum range, the PFs of n-type Bi$_2$Te$_3$ films always fluctuate in a wide range, reflecting a strong influence
due to manipulations of atomic defects and their density. In addition, the studies by Zhang et al.\textsuperscript{105} and Suh et al.\textsuperscript{134} have suggested that increasing the thickness of Bi$_2$Te$_3$ films has the effect of strengthening the in situ annealing from the heated substrate, which causes an apparent reduction in carrier concentration $n_e$ and the corresponding modification to the PF.

It is widely believed that the electronic transport properties of n-type Bi$_2$Te$_3$ films are controlled by V$_{Te}$ and Bi$_{Te}$ defects. As schematically illustrated in Figure 3G, their formation and transformation can be described by the following two equations:

$$2\text{Bi} + 3\text{Te} \rightarrow 2\text{Bi}_{\text{Te}} + (3 - x)\text{Te}_{\text{Te}} + x\text{Te} \uparrow + x\text{V}_{\text{Te}} + 2xe', \quad (1)$$

$$2\text{Bi}_{\text{Te}} + 5\text{V}_{\text{Te}} \rightarrow (2\text{V}_{\text{Te}}') + 3\text{V}_{\text{Te}} + 2\text{Bi}_{\text{Te}} + 12h, \quad (2)$$

in which the n-type V$_{Te}$ is formed under a Te-deficient condition, while the transformation of V$_{Te}$ to Bi$_{Te}$ will be caused by the thermal effect during the annealing process. The symbol $\uparrow$ in Equation (1) indicates the re-evaporation of Te from the heated substrates as vapors, leading to Te-deficient in the grown films. Apparently, the coexistence of V$_{Te}$ and Bi$_{Te}$ is inevitable in Bi$_2$Te$_3$ films, and this makes it difficult to eliminate the effect of p-type antisites Bi$_{Te}$ on the electronic properties of n-type films, specifically the bipolar effect that reduces $S$ and PF.\textsuperscript{135} To suppress the formation of V$_{Te}$ and Bi$_{Te}$, one needs to significantly increase the nominal Te content and promote the formation of n-type antisites Te$_{Bi}$ during the deposition of Bi$_2$Te$_3$ films. Zhang et al.\textsuperscript{101,105,131} and other researchers\textsuperscript{96,136} have shown that a low $T_{\text{sub}}$ (e.g., $\sim$250°C) and a high Te/Bi flux ratio (e.g., Te/Bi $\approx$ 18/1) are effective in promoting the formation of Te$_{Bi}$ and improving the $n_e$. The formation of Te$_{Bi}$ in Bi$_2$Te$_3$ films by increasing the nominal Te content can be expressed by the following formula,

$$5x\text{Te} + (2\text{Bi} + 3\text{Te}) \rightarrow 2\text{Bi}_{\text{Te}} + (3 + 3x)\text{Te}_{\text{Te}} + 2x\text{Te}_{\text{Bi}} + 2xe'. \quad (3)$$

In general, it is difficult to eliminate p-type antisites Bi$_{Te}$ during the growth of thin films, and the three types...
of atomic defects appear to be strongly coupled. Undoubtedly, this is a contributing factor to why the electronic properties of n-type Bi$_2$Te$_3$ films are difficult to reproduce, and why the PFs reported in most studies are low, having values no better than 1.0–1.5 mWm$^{-1}$K$^{-2}$. Figure 3H collects the best PFs measured on Bi$_2$Te$_3$ films from different reports. Based on the current studies, the best PF with n-type Bi$_2$Te$_3$ films is obtained when V$_{Te}$ or Te$_{Bi}$ are the dominant atomic defects. Under those conditions, the highest PF of 5.0 mWm$^{-1}$K$^{-2}$ was obtained at the carrier concentration of $\approx 10 \times 10^{19}$ cm$^{-3}$. Such a value of the PF is comparable to the best PF reported for bulk single crystals.$^{[124]}$

### 3.2 | Band bending and the optimization of carrier mobility

Figure 4A summarizes correlations between the electron density $n_e$ and carrier mobility $\mu$ of n-type Bi$_2$Te$_3$ thin films and bulk n-type Bi$_2$Te$_3$-based single crystals and polycrystals. N-type bulk Bi$_2$Te$_3$-based single crystals and polycrystals possess $\mu \approx 150$ cm$^2$V$^{-1}$s$^{-1}$, which is conspicuously superior to the mobility of 10–100 cm$^2$V$^{-1}$s$^{-1}$ in n-type Bi$_2$Te$_3$ films. This is rather surprising for the following two reasons. First, n-type Bi$_2$Te$_3$ films are usually single crystalline or possess a strong (00l) orientation, and thus should have comparable carrier mobility as bulk single crystals of the same composition. Second, single-crystalline p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ films possess a similar mobility as do bulk single crystals.$^{[137]}$

The results imply that an additional carrier scattering mechanism is at play in n-type Bi$_2$Te$_3$ films. Likely, its origin traces to the in situ transformation of V$_{Te}$ to Bi$_{Te}$ and to the band bending effect. Previous studies have reported on the surface band bending effect and on the thickness dependent electronic transport in TI Bi$_2$Se$_3$ films,$^{[138]}$ which suggests that the atomic defects may be distributed non-uniformly near the surface.

Suk et al. have found out that in n-type Bi$_2$Te$_3$ films the carrier concentration $n_e$ decreases by more than an order of magnitude as the film thickness increases from 10 to 1000 nm. Recently, Zhang et al. also noted the decreasing carrier concentration $n_e$ with the increasing film thickness as well as an abnormal change in the trend between the carrier concentration $n_e$ and the Seebeck coefficient $S$. For the first time, they observed an upward energy band bending from regions internal to the film surface, as shown in Figure 4B. The upward energy band bending was interpreted based on the following experimental findings. The bulk Fermi level, $E_F(SPB)$, derived from transport measurements is obviously higher than the surface $E_F$ determined from ARPES measurements. Based on the fact the films grew by the process of layer-by-layer growth, and due to the transformation of V$_{Te}$ to Bi$_{Te}$ as the films were in situ annealed, the band bending is presumed to result from a gradient distribution of atomic defects. That is, from the film surface to the film interior, the density of V$_{Te}$ gradually decreases, while the density of Bi$_{Te}$ increases.

**FIGURE 4** (A) Correlation between the electron density $n_e$ and the carrier mobility $\mu$ in n-type Bi$_2$Te$_3$. The data are collected from various reports on n-type Bi$_2$Te$_3$-based single crystals, bulk polycrystalline samples, and thin films. (B) The surface chemical potential $E_F$(ARPES) determined by ARPES measurements and the bulk Fermi level $E_F(SPB)$ calculated from transport properties as a function of film thickness for n-type Bi$_2$Te$_3$ films as well as a schematic showing the surface upward band bending. Reproduced from Ref. $^{[105]}$ Copyright 2020, AIP Publishing. (C) Schematic diagram of the built-in electric field-induced carrier scattering that has its origin in the gradient distribution of V$_{Te}$ and Bi$_{Te}$ defects along the film thickness direction. ARPES, angle-resolved photoemission spectroscopy.
and showed $m^* = 2.46 m_e$, $2.13 m_e$, and $1.50 m_e$ for films containing the dominating defects of V$_{Te}$, Te$_{Bi}$, and Bi$_{Te}$, respectively. Hence, the experimental analysis confirms that the formation of Bi$_{Te}$ brings with it a notably negative impact on the effective mass $m^*$ and thus on the Seebeck coefficient $S$ of n-type Bi$_2$Te$_3$. Moreover, the presence of p-type antisites Bi$_{Te}$ in n-type Bi$_2$Te$_3$ leads to the bipolar effect and the deterioration of $S$ and $PF$. The conspicuous degradation of the Seebeck coefficient in n-type Bi$_2$Te$_3$ by the presence of p-type carriers follows from a relation $S_{total} = (S_n + S_p)/(c_n + c_p)$, where $S_n$, $c_n$, and $S_p$, $c_p$ are the Seebeck coefficients and electrical conductivities of electrons and holes, respectively.$^{[115]}$

Figure 5B,C summarize the Seebeck coefficients as a function of electron density for n-type Bi$_2$Te$_3$-based films and bulk samples, respectively. The dotted lines in the figures represent the calculated Pisarenko curves with $m^* = 0.5 m_e$, $1.0 m_e$, and $2.0 m_e$. The $m^*$ of n-type Bi$_2$Te$_3$ films is mainly distributed in a wide range of $m^* = 1.0$–$2.0$ $m_e$, which is significantly larger than $m^* = 0.5$–$1.5$ $m_e$ in bulk counterparts. Peranii$^{[142]}$ and Deng et al.$^{[92]}$ have fabricated Bi$_2$Te$_3$ films with the increased density of V$_{Te}$ through adjusting $T_{sub}$, which resulted in a greatly increased $n_e$ and $m^* > 2.0 m_e$. Zhang et al.$^{[101]}$ have simultaneously optimized $T_{sub}$ and the ratio of Te/Bi, and found out that Bi$_2$Te$_3$ films with n-type antisites Te$_{Bi}$ as the dominant atomic defects possess enhanced $n_e$ and $m^* > 2.0 m_e$. Thermal annealing studies by Aabdin et al.$^{[66]}$ have shown that $n_e$ and $m^*$ have concurrently decreased during the annealing, while annealing at 250°C for 2 h resulted in a sharply reduced effective mass from $\sim 2.0 m_e$ to $\sim 0.5 m_e$. Large reductions in the carrier concentration and effective mass upon annealing are well explained by the transformation of V$_{Te}$ to Bi$_{Te}$, as previously discussed. Moreover, numerous experiments with bulk n-type Bi$_2$Te$_3$ show similar regulation characteristics.$^{[17,143,144]}$ Namely that the presence of n-type atomic defects, such as Te vacancies, V$_{Te}$, and Te$_{Bi}$ antisites in bulk n-type Bi$_2$Te$_3$ polycrystals$^{[14]}$ is beneficial for a simultaneous enhancement of their carrier concentration $n_e$ and the effective mass $m^*$, while the presence of p-type antisite defects Bi$_{Te}$ that form upon hot-forging or thermal annealing, is very detrimental for the electronic properties of bulk n-type Bi$_2$Te$_3$ polycrystalline samples.$^{[143]}$

In summary, numerous experiments have consistently documented that the low effective mass $m^*$ in n-type Bi$_2$Te$_3$-based thin films and bulk samples is associated with the presence of p-type Bi$_{Te}$ antisite defects, which also tend to enhance the highly detrimental bipolar heat conduction. Therefore, promoting and regulating the density of donor-like V$_{Te}$ and Te$_{Bi}$ defects while suppressing the formation of acceptor-like Bi$_{Te}$ defects, are crucial steps toward further optimization of the effective mass $m^*$, the
FIGURE 5  (A) Electronic structure at the conduction band edge measured at 10 K along both the $\Gamma$–K and $\Gamma$–M directions of Bi$_2$Te$_3$ films that contained V$_{Te}$, Te$_{Bi}$, and Bi$_{Te}$ as the dominant surface defects. Reproduced from Ref. [101] Copyright 2021, American Chemical Society. The Pisarenko plots and the $n_e$–S relationship at room temperature for Bi$_2$Te$_3$–based (B) films and (C) bulk samples

Seebeck coefficient $S$, and the power factor $PF$ of n-type Bi$_2$Te$_3$-based thin films and bulk structures.

4 | STRATEGIES TO OPTIMIZE THE ELECTRONIC PROPERTIES OF P-TYPE Bi$_2$Te$_3$-BASED THIN FILMS

In p-type Bi$_2$Te$_3$-based structures, regardless of whether bulk or thin films,[30–33] the optimal chemical composition is Bi$_{0.5}$Sb$_{1.5}$Te$_3$, where the large content of Sb ensures the p-type character of the structure. The optimization strategies focus on the manipulation of the hole density $n_p$ and on attaining the preferential orientation.

4.1 | Atomic defects engineering

Properly adjusting the substrate temperature $T_{sub}$ and the parameters of the postannealing process are the steps typically used to optimize the hole density $n_p$ and the power factor $PF$s of p-type Bi$_2$Te$_3$-based films. Figure 6A–D shows the room temperature $n_p$ and $PF$s as a function of $T_{sub}$ and $T_{ann}$. The $n_p$ does not show a clear variation with the substrate temperature $T_{sub}$.[145,146] In comparison, the annealing process seems to show a more definitive influence, the $n_p$ decreases with the increasing annealing temperature $T_{ann}$. The collected data suggest that, while the $n_p$ in Bi$_2$Te$_3$-based thin films is quite sensitive to the substrate and annealing temperatures, the actual values of $n_p$ vary greatly in different studies. Since the atomic defects in p-type Bi$_2$Te$_3$-based thin films are similar to those in n-type films, the defect engineering concerning p-type Bi$_2$Te$_3$-based films can be referred to Equations (1) and (2), as illustrated in Figure 6E. The increase of $T_{sub}$ and $T_{ann}$ will intensify the re-evaporation and sublimation of Te as well as the transformation of n-type V$_{Te}$ vacancies to p-type Bi$_{Te}$ and Sb$_{Te}$ antisite defects, leading to a concurrent increase in the density of V$_{Te}$, Bi$_{Te}$, and Sb$_{Te}$. Hence the change in the carrier concentration of holes $n_p$ depends on the relative density of n-type (V$_{Te}$) and p-type (Bi$_{Te}$ and Sb$_{Te}$) defects. Based on several studies reporting that $n_p$ increases significantly with the substrate temperature $T_{sub}$,[97,98] one may conclude that $T_{sub}$ is able to increase the density of p-type Bi$_{Te}$ and Sb$_{Te}$ antisite defects more than n-type V$_{Te}$ vacancies. An opposite conclusion can be reached regarding the effect of the annealing temperature $T_{ann}$. Meanwhile, as gleaned from Figure 6 and Table 2, the
optimized \( n_p \) is in the range of \( 2.7 - 7.5 \times 10^{19} \) \( \text{cm}^{-3} \), where the \( PF \) attains values \([91,104,106,109]\) better than 3.0 mWm\(^{-1}\) K\(^{-2}\).

4.2 | The effects of preferential orientation and fabrication methods

As illustrated in Table 2, the p-type Bi\(_2\)Te\(_3\)-based films with preferential orientations of (00l) and (0 1 5) can achieve excellent \( PFs \), in contrast to the n-type (00l)-oriented films. Therefore, it is instructive to discuss the magnitude of \( n_p \) and \( PFs \) of p-type films fabricated by different methods and having different preferential orientations, as depicted in Figure 7. First, different fabrication methods show a nearly identical influence on the tuning of the carrier concentration \( n_p \) in p-type films, where variations in the carrier concentration \( n_p \) of \( 1.0 - 30 \times 10^{19} \) \( \text{cm}^{-3} \) can be obtained. It is interesting to note that, the (00l)-oriented films attain higher \( n_p \) than the films with the (0 1 5)-orientation. Second, compared to the (0 1 5)-oriented films, the \( PFs \) measured on the (00l)-oriented films are distinctly superior, which is the consequence of higher carrier mobility \( \mu \) in the plane of the QLs. The best room temperature power factors of 5.3 and 3.8 mWm\(^{-1}\) K\(^{-2}\) are obtained in p-type films having (00l) and (0 1 5) preferential orientations and at the carrier concentrations of 7.5 and \( 2.7 \times 10^{19} \) \( \text{cm}^{-3} \),
respectively.\cite{106,109} Third, the p-type films achieve excellent PFs exceeding 2.0 mWm\(^{-1}\)K\(^{-2}\) regardless of the fabrication method. In view of limited reports in the literature and given a wide scatter in the experimental data, it would be worthwhile to redetermine the optimal thin film-processing window, including the determination of \(T_{\text{sub}}, T_{\text{ann}}\), and their temperature profiles, to obtain more consistent values of the power PFs in p-type Bi\(_2\)Te\(_3\)-based films.

## 5 | INTRIGUING TOPOLOGICAL PHENOMENA RELATED TO BI\(_2\)TE\(_3\)-BASED FILMS

As illustrated in Figure 1, Bi\(_2\)Te\(_3\)-based compounds are well-recognized 3D TIs characterized by the presence of fascinating topological surface states (TSS) that arise as a consequence of strong SOC and the ensuing band inversion. In principle, the highly mobile carriers in the TSS are not likely to play an important role in the TE performance of Bi\(_2\)Te\(_3\)-based compounds because the experimental realization of metallic TSS is contradictory to the requirements for a good TE material. Moreover, when the Fermi level \(E_F\) falls within the bulk band gap, the TSS are vastly overwhelmed by the bulk states in TIs.\cite{10,148} The highly mobile carriers within the TSS can make a meaningful contribution only if the film thickness is reduced down to the nanoscale range.\cite{138} Specifically, our previous study with insulating Bi\(_{0.64}\)Sb\(_{1.36}\)Te\(_3\) films\cite{149} has revealed that the TSS might very beneficially enhance the electrical conductivity \(\sigma\) and hence the \(PF\) as long as the film thickness is below 6 nm. At larger film thickness, the contribution from the TSS rapidly diminishes. Furthermore, during the past decade, Bi\(_2\)Te\(_3\)-based films have generated intensive attention in the field of condensed matter physics because of exciting discoveries of novel topological phenomena, particularly when the TIs contained magnetic elements\cite{71–77} or the topological state coupled with superconductivity.\cite{150–153}

### 5.1 | The QAH effect in Bi\(_2\)Te\(_3\)-based magnetic TIs

In magnetic TIs, the important QAH effect and the quantized Hall conductance associated with the dissipationless edge conduction states have been intensively explored in the past decade.\cite{49,154} Two prerequisites for the realization of the QAH effect are the opening of a magnetic gap at the DP via a long-range ferromagnetic order and the precise tuning of the Fermi level \(E_F\) into the gap, specifically the gapped Dirac surface states induced by intrinsic magnetism. Transition metals (Cr, Fe, and V)-doped Bi\(_2\)Te\(_3\)-based TIs and SLs of MnBi\(_2\)Te\(_4\), where a magnetic MnTe bilayer is intercalated into Bi\(_2\)Te\(_3\), have been theoretically predicted and experimentally verified as the prototype materials for demonstrating the fascinating QAH effect.\cite{72,74–77,154} ARPES-based band structure measurements, as well as the magnetotransport measurements made on Hall-bar devices, have provided direct experimental evidence for the existence of the QAH effect. The ARPES technique is very suitable and capable to distinguish the TSS, the DP, and the magnetic gap in Bi\(_2\)Te\(_3\)-based TIs and magnetic TIs, due to the high energy and angular resolution.\cite{155}

Figure 8A, B presents the ARPES-observed electronic band structure and the first magneto-electric evidence of the QAH effect for magnetic TIs doped with Fe (Bi\(_{0.84}\)Fe\(_{0.16}\))Se\(_3\) and with Cr Cr\(_x\)(Bi,Sb)\(_{2–x}\)Te\(_3\), respectively.\cite{72,75} The incorporation of the magnetic Fe dopant induces the ferromagnetic order in Bi\(_2\)Se\(_3\), and opens a magnetic gap at the DP that results from breaking the time-reversal symmetry. The ARPES spectrum at 10 K reveals a fundamental band gap of \(\sim 50\) meV in the energy-dispersive curve of (Bi\(_{0.84}\)Fe\(_{0.16}\))Se\(_3\).\cite{75} The decreasing size of the gap with the decreasing Fe content suggests its origin is tied to spontaneous magnetization. It is worth noting that the feature of in-gap DP makes Bi\(_2\)Se\(_3\) a better candidate to reveal the gap opening at the Dirac surface states than Bi\(_2\)Te\(_3\), where the DP is deep in the VBM.\cite{148} The ARPES verification of the magnetic gap and the characterization of magnetic properties were the essential steps enabling the discovery of the QAH effect by magneto-electrical measurements realized in the Cr- and V-doped (Bi,Sb)\(_2\)Te\(_3\) films.\cite{72,74} Intuitively, the QAH effect can be understood as an analog of the quantum Hall (QH) effect in the absence of an external magnetic field.\cite{136} The first experimental demonstration of the QAH effect was made in a 5-nm-thick MBE-grown Cr-doped Cr\(_{0.15}\)(Bi\(_{0.1}\)Sb\(_{0.9}\))\(_{1.85}\)Te\(_3\) film.\cite{72} Successful realization of the QAH in this material depended on the uniformly doped Cr in the structure and also on the proper location of the DP relative to the Fermi level \(E_F\) that was controlled by the content of Sb.\cite{157} To tune the Fermi level precisely within the magnetic gap, the authors relied on a gate voltage \(V_g\) via the dielectric SrTiO\(_3\) substrate. Following the above precision manipulations, two important signatures of the QAH effect were clearly observed.\cite{72} One was the manifestation of the quantized transverse Hall resistance \(\rho_{xy} \approx h/e^2\) accompanied by the dissipationless longitudinal electrical conductance \(\rho_{xx} \approx 0\) at zero field and the temperature of 30 mK when \(V_g = –1.5\) V. The other signature comprised the chirality reversal of edge conduction upon the corresponding reversal of magnetization field direction, which was
revealed by the sharp transition in $\rho_{yx}$ between $+h/e^2$ and $-h/e^2$, trigged by altering small positive and negative magnetic fields. Following shortly upon this study, the QAH effect was also successfully demonstrated in the V-doped (Bi,Sb)$_2$Te$_3$ film and in the modulation-doped Cr$_x$(Bi$_{0.1}$Sb$_{0.9}$)$_{1.85}$Te$_3$ film. The temperatures at which the QAH effect was observed were 25 and 500 mK for the above two structures, respectively.

In magnetically doped TIs, the QAH effect is restricted to subkelvin temperatures and, as such, is not very promising for future device applications.\[157,159\] To realize the QAH effect at higher temperatures, an intrinsic magnetic TI structure of MnBi$_2$Te$_4$ was recently proposed and intensively studied.\[76,77,139,160,161\] On the one hand, the MnTe bilayer ensures a robust ferromagnetic order for the individual MnBi$_2$Te$_4$ septuple layer, while the adjacent septuple layers are coupled antiferromagnetically, forming A-type antiferromagnetic ordering in bulk MnBi$_2$Te$_4$. On the other hand, and in contrast to the case of magnetically doped TIs, the SL-like MnBi$_2$Te$_4$ structure seems to suppress the inhomogeneous doping on the atomic scale and thus the spatial magnetic fluctuations. Figure 8C,D displays the ARPES spectrum and the magneto-electric transport results of MnBi$_2$Te$_4$.\[76,77\] The clear linearly dispersing TSS indicates the magnetic TI characteristics of MnBi$_2$Te$_4$. Strong sensitivity of the TSS on the antiferromagnetic ordering further verifies this, as revealed by the temperature-dependent photoemission intensity of the TSS.\[77\] Moreover, studies from several other groups have repeatedly verified the gapless nature of TSS in MnBi$_2$Te$_4$, which is contrary to the theoretically predicted magnetic gap that should have been induced by the intrinsic antiferromagnetic ordering.\[162-166\] This unsolved problem likely results from the complex magnetic structure near the surface and from the poor structural stability of the material, and requires further study. The odd and even numbers of septuple layers impose extraordinary influence on the magnetic properties of MnBi$_2$Te$_4$ thin films, due to the competition of...
odd-layer number thick ferromagnetic and even-layer number thick antiferromagnetic strata with completely canceled magnetization.\textsuperscript{167,168} Thus, the odd-layer number thick MnBi\textsubscript{2}Te\textsubscript{4} film is supposed to be the appropriate platform for realizing the QAH effect. As depicted in Figure 8D, the 5 septuple-layer thick MnBi\textsubscript{2}Te\textsubscript{4} device exhibits the zero-field QAH effect at 1.4 K, that is, the quantized $\rho_{yx}$ and the dissipationless $\rho_{xx}$ at $V_g = -200$ V, which is significantly superior with its an order of magnitude larger values than what has been obtained in magnetically doped (Bi,Sb)\textsubscript{2}Te\textsubscript{3} films.\textsuperscript{76} Furthermore, experiments with 6 and 10 septuple-layer thick MnBi\textsubscript{2}Te\textsubscript{4} devices have revealed that these even-layer number thick films are transformed from the axion insulator phase to the Chern insulator phase with quantized $\rho_{yx}$ and dissipationless $\rho_{xx}$ at low temperatures and high magnetic fields (similar to the QH effect).\textsuperscript{160,161}

5.2 Proximity effects in Bi\textsubscript{2}Te\textsubscript{3}-based heterostructures

The proximity effect is a very effective approach to tailoring novel physical properties of low-dimensional materials through interactions with the neighboring regions.\textsuperscript{169} This section focuses on the proximity-induced profound alteration of SOC and the unconventional nature of superconductivity in Bi\textsubscript{2}Te\textsubscript{3}-based heterostructures. Figure 9A,B depict the tendency of a topological nontrivial band gap opening in graphene and in a monolayer of 1T'-MoTe\textsubscript{2} when interfaced with Bi\textsubscript{2}Te\textsubscript{3} and Bi\textsubscript{2}Te\textsubscript{3} layers, respectively. Graphene is regarded as a 2D TI that hosts the quantum spin Hall (QSH) state and the dissipationless edge transport, while its bulk band gap is too small to be observed due to the carbon’s small atomic number and very weak SOC.\textsuperscript{170,171} The SOC proximity effect is an alternative approach to increase the SOC gap of graphene upon forming a heterostructure, as documented in the graphene/Bi\textsubscript{2}Te\textsubscript{3}Se heterostructure.\textsuperscript{172,173} As shown in Figure 9A,\textsuperscript{173} the enhancement of the SOC gap in graphene is induced by a resonance-type proximity effect without sacrificing the intrinsic feature of graphene, specifically the linear band dispersion. Through the dose of Cs on the surface of the heterostructure, two DPs of graphene and Bi\textsubscript{2}Te\textsubscript{3}Se were brought together in energy due to the charge transfer from Cs atoms to graphene. As a result, a fundamental SOC gap of $\sim$20 meV was obtained when the two DPs nearly coincided in energy. However, these theoretical calculations were not exactly verified by experiments because the ARPES spectra became very blurred upon dosing Cs on the surface of graphene. The other example shows the tendency of a band gap opening in a monolayer of 1T'-MoTe\textsubscript{2} grown on the Bi\textsubscript{2}Te\textsubscript{3} buffer layer\textsuperscript{174} as illustrated in Figure 9B. The monolayer 1T'-MoTe\textsubscript{2} is predicted to be a promising QSH phase, however, the pristine monolayer 1T'-MoTe\textsubscript{2} is a semimetal with the negative band gap.\textsuperscript{175,176} The strain engineering, that is, an artificial tuning of the lattice parameters, was theoretically predicted to separate the valence and conduction bands and hence lead to an opening of a positive band gap, the situation not yet verified experimentally.\textsuperscript{177} Our group has recently proposed a plausible road for the opening of the band gap in a monolayer of 1T'-MoTe\textsubscript{2} through the formation of a 1T'-MoTe\textsubscript{2}/Bi\textsubscript{2}Te\textsubscript{3} vdW-type heterostructure and by utilizing the SOC proximity effect.\textsuperscript{174} Our theoretical studies have revealed that strong interfacial interactions and the prominent charge transfer at the interface are the origins of the SOC proximity effect and the enhanced intrinsic SOC in such a heterostructure. The enhanced intrinsic SOC is the prerequisite for the band gap opening, and the calculated band gap for a monolayer of 1T'-MoTe\textsubscript{2} is $\sim$40 meV. Nevertheless, the experimental ARPES and STM results have confirmed the tendency to separate the conduction and valence bands, while a full band gap is not expected to materialize in a monolayer of 1T'-MoTe\textsubscript{2} grown on Bi\textsubscript{2}Te\textsubscript{3}. The discrepancy between the calculated and experimental results should be ascribed to effects other than the SOC proximity, for example, to the strain engineering and the interfacial Rashba effect.\textsuperscript{169,177}

It is theoretically predicted that the superconducting TIs may harbor the intriguing Majorana fermions that are intensively studied for their importance to fundamental science and to potential applications in quantum computing.\textsuperscript{150–153} The superconducting proximity effect is an effective way to create a superconducting TI, which was first proposed by Fu and Kane and experimentally realized by others.\textsuperscript{150,153,178,179} The vdWs growth of topological Bi\textsubscript{2}Se\textsubscript{3} and Bi\textsubscript{2}Te\textsubscript{3} thin layers on superconducting NbSe\textsubscript{2} substrates is a prospective approach toward the goal of realizing Majorana fermions because the structure benefits from perfectly layered strata and negligible interfacial interactions. Figure 9C shows the surface morphology of Bi\textsubscript{2}Se\textsubscript{3} thin films grown on NbSe\textsubscript{2} substrates as well as the superconducting energy gap (at 4.2 K) observed in Bi\textsubscript{2}Se\textsubscript{3} films.\textsuperscript{153} A Bi (110)-oriented bilayer is first deposited on the NbSe\textsubscript{2} substrate, and serves as a buffer layer for the deposition of atomically flat Bi\textsubscript{2}Se\textsubscript{3} films, with the surface being covered by 2 QLs Bi\textsubscript{2}Se\textsubscript{3} films. The differential conductance (dI/dV) spectra were obtained via scanning tunneling spectroscopy (STS) measurements and document the presence of superconducting energy gaps ($\Delta$) of bare NbSe\textsubscript{2} and Bi\textsubscript{2}Se\textsubscript{3} grown on the NbSe\textsubscript{2} substrate. The gap parameters were
acquired by fitting the STS spectra using the Bardeen–Cooper–Schrieffer-like tunneling spectrum function. The sizable value of Δ suggests that the Bi₂Se₃ films turn superconducting due to the superconducting proximity effect from the NbSe₂ substrate. The superconducting state of Bi₂Se₃ films was further confirmed by STS measurements under a magnetic field in which the superconducting gap Δ has greatly diminished in the increasing magnetic field. The fitted Δ, as a function of the film thickness, is in a qualitative agreement with the theoretical analysis based on the proximity effect. The apparent linear band dispersion of TSS (from ARPES measurements) and the sizable Δ (from STS measurements) depict the coexistence of superconductivity and topologically nontrivial state in the Bi₂Se₃ layers of the Bi₂Se₃/NbSe₂ heterostructure. Subsequent ARPES
measurements performed at ultralow temperatures confirmed the topological superconducting state in the Bi$_2$Se$_3$/NbSe$_2$ heterostructure.$^{[180]}$ Therefore, the Bi$_2$Se$_3$/NbSe$_2$ heterostructure and similar structures provide an ideal platform for the realization and study of the exotic properties of Majorana-bound states and are currently intensively pursued worldwide.

6 | Bi$_2$Te$_3$-BASED THIN FILM TE DEVICES

Compared to their bulk counterparts, integration of Bi$_2$Te$_3$-based thin films with flexible substrates and the use of micromachining processes offer distinct advantages during the fabrication of flexible miniaturized TE devices. The current experience with the existing miniature TE coolers and power generators indicates that the Bi$_2$Te$_3$-based thin films have a tremendous application potential as active TE coolers in many electronic devices and as TE heat harvesters and converters where very small temperature gradients occur, such as in wearable electronic gadgets.$^{[1,3,8,181]}$ Specific examples include the site-specific and on-demand cooling in silicon chips$^{[3]}$ as well as the self-powered skin attachable intelligent devices.$^{[181]}$ The maximum cooling flux ($q_{\text{max}}$) and the power output ($P_{\text{max}}$) for a TE device are given by

$$q_{\text{max}} = \frac{(S_p - S_n)T_cT_f}{4(\rho_n + \rho_p)l},$$

$$P_{\text{max}} = \frac{(S_p - S_n)(T_h - T_c)^2A}{4(\rho_n + \rho_p)l},$$

where $S_p$ and $\rho_p$ as well as $S_n$ and $\rho_n$ are Seebeck coefficients and electrical resistivities of p- and n-type TE legs, respectively.$^{[126,182,183]}$ To achieve high $q_{\text{max}}$, the PF of TE films must be high, while the filling factor ($f$) of a TE module and the thickness ($l$) of TE legs should be, respectively, large and as small as possible. The $P_{\text{max}}$ of TE films is directly proportional to the PF and the temperature difference ($T_h - T_c$), and is also related to the ratio of the cross-section area ($A$) and the length ($l$) of TE legs. Table 3 summarizes the prominent performances of Bi$_2$Te$_3$-based thin films devices. According to Equation (4), a device using the vertically structured TE films is suitable for active cooling applications chiefly due to the small, nanometer-scale leg thickness $l$. Cooling devices based on p-type SLs and n-type BiTeSe with the vertical structure have been reported$^{[1,3,83]}$ with the highest $q_{\text{max}}$ of 258–1300 Wcm$^{-2}$, verifying the positive effect of small leg thickness $l$ and the large power factor. In contrast, cooling devices fabricated from p-type Te and n-type BiTeSe, deposited by the ECD process, attained a couple of orders lower magnitude$^{[6]}$ of $q_{\text{max}} \approx 5.8$ Wcm$^{-2}$. Such poor cooling performance resulted from an inferior operation of both TE legs and from large parasitic electrical and thermal contact resistances. Furthermore, a three-stage vertical SL-based device pumped heat more efficiently than a single-stage device due to the cooperative cooling of the individual stages, and such a multistage cooler achieved the maximum cooling of 101.6 K at the cold side,$^{[184]}$ with the hot junction maintained at about 300 K. Referring to Equation (5), the $P_{\text{max}}$ is directly proportional to the square of the temperature difference $T_h - T_c$ across the device and to the cross-sectional area of the legs $A$. Thus, a large $T_h - T_c$ and a thick film usually lead to an optimal $P_{\text{max}}$ on the order of $\mu$W for Bi$_2$Te$_3$-based thin film TE devices$^{[182,183,185,186]}$, which is sufficient to meet the power supply requirements of low power electronics. Figure 10 illustrates an application of (a) active cooling and of (b) a self-powered electronic device based on thin-film TE devices. The first example also displays the micro-machining processing steps needed to assemble a thin film TE cooler, which is compatible with the fabrication processes used in microelectronics.$^{[3]}$ It was reported that$^{[3]}$ localized cooling by as much as 15 K and an ultrahigh $q_{\text{max}}$ of $\sim$1300 Wcm$^{-2}$ can be achieved in an actual silicon chip package by Bi$_2$Te$_3$ SL-based thin film TE coolers. In comparison, the $q_{\text{max}}$ of bulk devices$^{[183]}$ is on the order of 10 Wcm$^{-2}$. The ultrahigh $q_{\text{max}}$ achieved with Bi$_2$Te$_3$ SL-based thin film TE coolers demonstrated that such coolers are effective and crucial for cooling the localized hotspots with ultrahigh heat flux in various types of electronic devices. The second example documented the success of a self-powered wearable pressure sensing system fully powered by a flexible thin-film TE power generator.$^{[183]}$ Three features contributed to its excellent performance. First, the n-type Bi$_2$Te$_3$ and p-type Sb$_2$Te$_3$ films with optimized room temperature $PFs$ of 0.87 and 1.86 mWm$^{-1}K^{-2}$, respectively, were fabricated for this application via a controllable MS process. Second, the polyamide substrate, the PDMS/BN heat absorber, and the hydrogel heat sink provided excellent structural flexibility of the integrated device. Third, insulating films of the PDMS/BN composite and hydrogel possessed high thermal conductivity, resulting in a large $T_h - T_c$ and thus a high $P_{\text{max}}$. In the real flexible thin-film TE device, a $P_{\text{max}}$ of 7.9 $\mu$W was reached for $T_h - T_c$ of 20 K. Attaching such an integrated device to a human body has
demonstrated that the real-time monitoring of diverse physiological signals and body motions is possible via harvesting the body heat as a power source for the device.

### 7 | CONCLUSION AND PERSPECTIVES

Bi$_2$Te$_3$-based thin films have shown fascinating physical properties and very important application prospects in the field of thermoelectricity and in supplying power for the next generation of low power electronics and in quantum computation. As an example, thin-film TE devices based on high-performance Bi$_2$Te$_3$-based films are the key prerequisite for the fabrication of flexible and miniaturized electronic devices that require highly effective site-specific and on-demand active cooling and for their self-powered power supplies. The intriguing QAH effect discovered in the Bi$_2$Te$_3$-based magnetic TIs provides a new feasible approach to realize dissipationless edge transport could be applied in low-power electronic circuits similar to the QH effect, but without applying a magnetic field. The proximity superconductivity in the Bi$_2$Te$_3$-based TI/superconductor heterostructures offers an ideal platform for detecting the elusive Majorana fermions that are proposed to be potential building blocks of quantum computation. Despite the considerable progress made in recent years, the exploration of new physical mechanisms and applied technologies regarding Bi$_2$Te$_3$-based thin films must continue in full force to realize new breakthroughs in their intriguing physical properties and to prepare the path for their successful commercial applications.

| TABLE 3 | Summary of the performances of typical Bi$_2$Te$_3$-based thin-film thermoelectric devices listed in previous reports
| --- | --- |
| **Thin-film thermoelectric cooling devices** |  |
| Year | Materials | Type | Material thickness | Lateral dimension | $f$ | $\Delta T$ (K) | $q$ (W cm$^{-2}$) |
| 2001$^{[82]}$ | p-Type SL n-type BiTeSe | Vertical | 5.4 $\mu$m | – | – | 32 | 585 |
| 2009$^{[8]}$ | p-Type SL n-type BiTeSe | Vertical | 5–8 $\mu$m | $3.5 \times 3.5$ mm$^2$ | – | 15 | 1300 |
| 2016$^{[83]}$ | p-Type SL n-type BiTeSe | Vertical | 8.1 $\mu$m | $0.6 \times 0.6$ mm$^2$ | 48% | 44 | 258 |
| 2018$^{[84]}$ | p-Type SL n-type BiTeSe | Vertical | 10 $\mu$m | $2 \times 2$ mm$^2$ | 20% | 5–12 | 5.8 |
| 2009$^{[85]}$ | p-Type SL n-type BiTeSe | Three stage | 2.5 mm | mm$^2$ Scale | – | 102 | – |
| 2014$^{[86]}$ | p-Bi$_{0.5}$Sb$_{1.5}$Te$_3$ n-Bi$_2$Te$_2$Se$_{0.3}$ | Vertical | 2 $\mu$m | mm$^2$ Scale | 21% | 14.6 | – |
| 2013$^{[87]}$ | n-Bi$_2$Te$_3$ | Lateral | 1–4 $\mu$m | $22 \times 10$ mm$^2$ | – | 3.2 | – |
| 2015$^{[88]}$ | p-Bi$_{0.5}$Sb$_{1.5}$Te$_3$ | Lateral | 150 $\mu$m | $20 \times 60$ mm$^2$ | 6.4 | – | – |

| **Thin film thermoelectric power generation devices** |  |
| Year | Materials | Type | $\Delta T$ (K) | Material thickness | Area (cm$^{-2}$) | Power ($\mu$W) | Power density ($\mu$W/cm$^2$) |
| 2011$^{[89]}$ | p-Sb$_2$Te$_3$ n-Bi$_2$Te$_3$ | Lateral | 40 | – | 21 | 0.032 | – |
| 2011$^{[90]}$ | p-Sb$_2$Te$_3$ | Lateral | 106 | 3 $\mu$m | 2.1 | 6.51 | – |
| 2013$^{[91]}$ | n-Bi$_2$Te$_3$ | Lateral | 81 | 2 $\mu$m | 2.1 | 6.53 | 43000 |
| 2014$^{[92]}$ | p-Bi$_{0.5}$Sb$_{1.5}$Te$_3$ n-Bi$_2$Te$_2$Se$_{0.3}$ | Vertical | 4 | 2 $\mu$m | 1.98 | 145.2 | 73.3 |
| 2015$^{[93]}$ | p-Sb$_2$Te$_3$ n-Bi$_2$Te$_3$ | Vertical | 39.7 | 12 $\mu$m | – | 1100 | 3840 |
| 2016$^{[94]}$ | p-Sb$_2$Te$_3$ n-Bi$_2$Te$_3$ | Lateral | 4.9 | 10 $\mu$m | – | 0.034 | – |
| 2017$^{[95]}$ | p-Bi$_{0.5}$Sb$_{1.5}$Te$_3$ n-Bi$_2$Te$_3$ | Lateral | 18.2 | 1 $\mu$m | 25 | 18.2 | – |
| 2019$^{[96]}$ | p-Sb$_2$Te$_3$ n-Bi$_2$Te$_3$ | Lateral | 70 | – | $\sim$18 | 23.6 | – |
| 2020$^{[97]}$ | p-Bi$_{0.5}$Sb$_{1.5}$Te$_3$ n-Bi$_2$Te$_3$ | Lateral | 40 | 0.42 $\mu$m | $\sim$4.5 | 0.16 | 897.8 |
| 2020$^{[98]}$ | n-Bi$_2$Te$_3$/SWCNT hybrid | Lateral | 25 | 0.18 | $\sim$2.1 | 55 | 930 |
| 2020$^{[99]}$ | p-Sb$_2$Te$_3$ n-Bi$_2$Te$_3$ | Lateral | 20 | 2–4 $\mu$m | – | 7.9 | – |
Optimizing the TE performance: The most studied n-type Bi$_2$Te$_3$ and p-type (Bi,Sb)$_2$Te$_3$ films attain the best PF of 3.5–5.0 mWm$^{-1}$K$^{-2}$ via the optimization of atomic intrinsic defects and preferential orientation. However, the repeatability of measurements reporting high TE performance is not satisfactory. A deep understanding of all tuning mechanisms that regulate the film growth and lead to an outstanding TE performance is of paramount importance. Specifically, the high ZTs of Bi$_2$Te$_3$-based films not only require excellent PFs but also strongly rely on a very low lattice thermal conductivity $\kappa_L$. Defect engineering in combination with the design and fabrication of suitable superlattice structures are essential for obtaining Bi$_2$Te$_3$-based films with further, significantly improved ZT values.

FIGURE 10  Thermoelectric cooling and power generation performance of thin films. (A) Fabrication steps for the Bi$_2$Te$_3$-based superlattice thermoelectric coolers and their cooling performance. The final 7 x 7 thermoelectric array (3.5 x 3.5 mm$^2$) is attached to a silicon chip for testing its cooling performance by withdrawing heat from a nearby localized hot spot. The total (passive and active) localized cooling of 14.9°C can be achieved by passing a DC current of ~3 A. Modeling shows that the thermal contact resistance degrades the cooling performance more than the electrical contact resistance. Reproduced from Ref. [3] Copyright 2009, Springer Nature. (B) Schematic description and film morphology of the self-powered wearable pressure sensing system that integrates a Bi$_2$Te$_3$-based thin film power generator with a flexible pressure sensor, as well as the performance of the thin-film power generator. An output voltage of 78 mV and a maximum power of 7.9 $\mu$W can be achieved at a temperature gradient of 20 K across the device. A thin heater absorber (PDMS/BN) together with the application of a heat sink (hydrogel) is beneficial for maintaining a large temperature gradient across the device. PDMS/BN, Polydimethylsiloxane/Boron nitride composite. Reproduced from Ref. [183] Copyright 2020, Elsevier.
(2) **TE applications**: Bi$_2$Te$_3$-based thin films are amenable to being fabricated as flexible and miniaturized TE devices. In general, the vertical structure of thin-film TE devices is beneficial for cooling applications as it yields very high $q_{\text{max}}$, while the parallel structure is good for power generation with large $P_{\text{max}}$. It is important to develop thin-film TE devices from high TE performance Bi$_2$Te$_3$-based thin films to efficiently pump heat fluxes and harvest thermal energies. Meanwhile, minimizing the interfacial contact electrical and thermal resistances between TE films and metal electrodes is of equal importance for fully functional integrated TE thin-film devices.

(3) **Intriguing topological phenomena**: The QAH effect and the SOC/superconducting proximity effect revealed in Bi$_2$Te$_3$-based magnetic TIs and heterostructures are currently hot topics in the condensed matter physics. To fabricate reliably MnBi$_2$Te$_4$-based thin films is the essential step toward the potential application of the QAH effect. The deep physical insight into the SOC/superconducting proximity effect will enable the discovery of new TI phases as well as their rational design and manipulation.

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**CONFLICT OF INTERESTS**

The authors declare that there are no conflict of interests.

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