PAPER

Tuning thermoelectricity in a Bi$_2$Se$_3$ topological insulator via varied film thickness

Minghua Guo$^{1,7}$, Zhenyu Wang$^{1,7}$, Yong Xu$^{1,2,3,7}$, Huaqing Huang$^{1}$, Yunyi Zang$^{1}$, Chang Liu$^{1}$, Wenhui Duan$^{1,2,4}$, Zhongxue Gan$^{3}$, Shou-Cheng Zhang$^{1,8}$, Ke He$^{1,2}$, Xucun Ma$^{5,6}$, Qikun Xue$^{1,2}$ and Yayu Wang$^{2}$

$^1$ State Key Laboratory of Low Dimensional Quantum Physics, Department of Physics, Tsinghua University, Beijing 100084, People’s Republic of China
$^2$ Collaborative Innovation Center of Quantum Matter, Beijing 100084, People’s Republic of China
$^3$ RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan
$^4$ Institute for Advanced Study, Tsinghua University, Beijing 100084, People’s Republic of China
$^5$ ENN Intelligent Energy Group, ENN Science Park, Langfang, Hebei 065001, People’s Republic of China
$^6$ Department of Physics, Stanford University, Stanford, CA 94305–4045, USA
$^7$ These authors contributed equally to this work.
$^8$ E-mail: kehe@tsinghua.edu.cn and yayuwang@tsinghua.edu.cn

Keywords: topological insulator, thermoelectricity, transport, Seebeck coefficient

Abstract

We report thermoelectric transport studies on Bi$_2$Se$_3$ topological insulator thin films with varied thickness grown by molecular beam epitaxy. We find that the Seebeck coefficient and thermoelectric power factor decrease systematically with the reduction of film thickness. These experimental observations can be explained quantitatively by theoretical calculations based on realistic electronic band structure of the Bi$_2$Se$_3$ thin films. This work illustrates the crucial role played by the topological surface states on the thermoelectric transport of topological insulators, and sheds new light on further improvement of their thermoelectric performance.

Introduction

The solid-state thermoelectric technologies, which enable the direct conversion of thermal and electrical energies with the advantages of being quiet, reliable, scalable and eco-friendly, are expected to play an important role in meeting the global energy and environmental challenges [1–4]. Widespread applications of thermoelectricity require the improvement in the efficiency of the thermoelectric devices. The performance of a thermoelectric material can be characterized by a dimensionless figure of merit defined as $ZT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $T$ and $\kappa$ are the Seebeck coefficient (thermopower), electrical conductivity, absolute temperature and thermal conductivity, respectively. The quantity $S^2\sigma$ is called the power factor, which characterizes the ability of electrons in the thermoelectric material for energy output under a given temperature difference. The main approaches for enhancing $ZT$ are either by maximizing the power factor and/or minimizing the thermal conductivity [5].

Quantum confinement introduced by low-dimensionality was proposed to be an efficient method for enhancing the power factor and suppressing the phonon thermal conductivity simultaneously [2, 6, 7]. It was predicted that in Bi$_2$Te$_3$ thin films, $ZT$ can be significantly enhanced by reducing the film thickness [6]. In recent years, it was discovered that the best room temperature thermoelectric materials such as Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are three-dimensional (3D) topological insulators (TI) with inverted bulk band structure and topologically protected metallic surface states [8–10]. Therefore, the topological surface states must be taken into account when considering the thermoelectric properties of TIs, especially in the thin limit. It has been proposed theoretically that in TI thin films, the thermoelectric contributions from the parallel bulk and surface channels tend to cancel each other because the bulk and surface $ZT$s are optimized at different Fermi levels ($E_F$s). As the
film becomes thinner, $ZT$ would not be enhanced dramatically, but a decent increase could still be observed when the $E_F$ lies in an optimal position [11].

The thermoelectric properties of $\text{Bi}_2\text{Te}_3$ family TI thin films have been experimentally investigated recently. By using the band structure engineering method to fine tune the $E_F$ of TI, it was found that the thermopowers of $(\text{Bi}_1-x\text{Sb}_x)\text{Te}_3$ ternary thin films do not show any improvement from the bulk value over a wide range of $E_F$ positions. Instead, it exhibits a peculiar sign anomaly with the Hall effect induced by the drastically different transport properties of the bulk and surface states [12]. In a more recent study of $p$-type $\text{Sb}_2\text{Te}_3$, TI thin films [13], it was found that tuning the $E_F$ position and film thickness has a significant impact on the total thermopower, also demonstrating the effect of topological surface states on the thermoelectric properties of TI.

In this work, we investigate the thermoelectric properties of the $n$-type $\text{Bi}_2\text{Se}_3$ TI thin films with different thicknesses grown by molecular beam epitaxy (MBE). As the film thickness is reduced from $d = 30$ QL (quintuple layer) to 5 QL, the thermopower as well as the power factor decreases systematically. This is mainly because the linear electron band dispersion of the Dirac-like surface state is not optimal for thermopower, which prefers an abrupt change of electron density of states (DOS) near the $E_F$ [14]. With decreasing thickness, the growing contribution of the surface state reduces the total thermopower and the power factor. Another effect is the change of $E_F$ position with film thickness, which mainly affects the bulk thermopower and the relative contribution of the surface states. These results can be explained quantitatively by theoretical calculations based on the realistic electronic band structures of $\text{Bi}_2\text{Se}_3$ TI thin films, and shed new light on future improvement of the thermoelectric performance of TI.

**Methods**

A. **MBE sample growth:** The $\text{Bi}_2\text{Se}_3$ thin films are grown on insulating $\text{SrTiO}_3$ (111) substrates ($2 \times 8 \times 0.25$ mm) in an ultra-high vacuum MBE system with a base pressure lower than $1 \times 10^{-10}$ mbar. Before the sample growth, the $\text{SrTiO}_3$ substrates are degassed at 300 °C for 30 min. High-purity Bi (99.999%) and Se (99.999%) sources are evaporated from standard effusion cells. To reduce the number of Se vacancies, the growth is kept in an Se-rich condition with the substrate temperature kept at 180 °C.

B. **ARPES measurements:** The in situ angle-resolved photoemission spectroscopy (ARPES) measurements are carried out at 77 K by using a Scienta R4000 electron energy analyzer. A Helium discharge lamp with a photon energy of $h\nu = 21.2$ eV is used as the photon source. The energy resolution of the electron is 10 meV, and the angle resolution is 0.2°. All the spectra shown in the paper are taken along the K-Γ-K direction.

C. **Transport measurements:** Figure 1(a) shows the schematic setup of the transport measurements on the $\text{Bi}_2\text{Se}_3$ thin films. The resistance and thermopower measurements are performed on the same area in the central part of the $\text{Bi}_2\text{Se}_3$ thin film. Electrical transport properties are measured in an isothermal condition using the delta mode of the Keithley 6221 current source plus the 2182A nanovoltmeter. Thermoelectric measurements are carried out in the high-vacuum condition with pressure lower than $1 \times 10^{-6}$ mbar. The temperature gradient is produced by a thin-film heater mounted on the right end of the substrate. A pair of fine-gauge thermocouples (type E, CHROMEGA/constantan) are connected in subtractive series and
thermally anchored to the substrate to monitor the temperature difference across the sample. The dc voltages of the Seebeck effect and thermocouples are recorded by Keithley 2182A nanovoltmeters.

D. Theoretical calculations: First-principles electronic structure calculations were performed within the framework of density functional theory (DFT) as implemented in the Vienna ab initio simulation package [15]. The projector-augmented-wave potential, the plane-wave basis with an energy cutoff of 210 eV, and the Perdew–Burke–Ernzerhof [16] exchange-correlation functional in the generalized-gradient approximation were used in DFT calculations including the spin–orbit coupling effect. To study thermoelectric properties of Bi$_2$Se$_3$ thin films, band structure on a dense $k$ grid of $200 \times 200 \times 1$ was computed with the help of the Wannier-interpolation technique. The Wannier90 package [17] was used to construct the maximally localized Wannier functions (MLWFs) [18, 19] from DFT slab calculations, and then a tight-binding Hamiltonian was built from MLWFs to calculate band structure on a dense $k$ grid at a much smaller computational cost [20]. Thermoelectric properties were studied by the Landauer transport approach [21, 22] with the constant mean-free-path model [21]. The electron transmission function is equal to the density of modes $M(E)$ (i.e. the number of conduction channels per width) times the transmission probability, $M(E)$ was calculated by counting conduction channels from the band structure in the whole Brillouine zone. The transmission probability is proportional to the mean free path (MFP) in the diffusive limit [21, 23, 24]. Two constant MFPs $l_s$ and $l_b$ are required to describe the TI surface and bulk states, respectively. In our calculations of the Seebeck coefficient, the only free parameter is the MFP ratio $r = l_s/l_b$, which was determined by fitting the experimental data. For Bi$_2$Se$_3$ TI thin films, $M(E)$ can be separated into

Figure 2. Temperature dependence of 2D sheet resistance $R_S$, Seebeck coefficient $S$ and thermoelectric power factor $S^2\sigma$ for the Bi$_2$Se$_3$ thin films with different thicknesses. (a) The sheet resistances of the Bi$_2$Se$_3$ thin films show metallic behavior at high $T$ and turn to weakly insulating at very low $T$. With the decrease of film thickness, the $R_S$ value keeps rising and the insulating tendency becomes stronger. (b) The Bi$_2$Se$_3$ thin film shows a negative Seebeck coefficient with a quasi-linear $T$ dependence. The absolute value of $S$ decreases very systematically with decreasing thickness. (c) The power factor drops significantly with reducing film thickness.
the surface and bulk parts according to the band dispersion, and the surface contribution $M_s(E)$ was calculated from the Dirac–like bands.

**Results and discussions**

To investigate the thickness dependence of the thermoelectric performance of TI thin films, Bi$_2$Se$_3$ thin films are prepared with varied thicknesses including $d = 5, 7, 10, 15, 20$ and $30$ QL. Shown in figures 1(b) to (d) are the ARPES band maps of the 7, 10 and 20 QL Bi$_2$Se$_3$ thin films, respectively. In all three samples the $E_F$ cuts through the bulk conduction bands (BCBs) due to the existence of electron-type bulk carriers donated by Se vacancies during sample growth. The Dirac–like topological surface states with linear band dispersion can be clearly observed in all samples. For the 7 QL sample, the $E_F$ lies at around 0.11 eV above the bottom of BCB and 0.34 eV above the Dirac point of the surface state. With increasing film thickness, the $E_F$ position is lowered towards the Dirac point due to the decrease of Se vacancy density in thicker films, which has a better crystalline quality as the Bi$_2$Se$_3$ layers move further away from the rather rough substrate surface. For $d = 10$ QL and 20 QL, the $E_F$ positions are about 0.025 eV and 0.020 eV above the BCB minimum, which are nearly the same. Therefore the change of $E_F$ position becomes much smaller for films thicker than 10 QL. This is very reasonable from the MBE sample growth perspective because when the film is sufficiently thick, the influence of the substrate becomes negligible.

Figure 2 displays the temperature dependence of the two-dimensional (2D) sheet resistance $R_{2D}$, the Seebeck coefficient $S$ and the power factor $S^2\sigma$ for six Bi$_2$Se$_3$ thin films with different thicknesses. The resistances of all Bi$_2$Se$_3$ thin films (figure 2(a)) show a metallic behavior at high temperature and turn to weakly insulating at a very low temperature. This is the typical behavior of Bi$_2$Se$_3$ thin films in the 2D limit caused by the electron–electron interaction effect in the presence of disorders [25]. When the film thickness decreases from 30 QL to 5 QL, the $R_{2D}$ value keeps rising and the insulating tendency is enhanced. On the one hand, this is due to the degradation of sample quality, hence electron mobility, as the film becomes thinner. On the other hand, this reflects the decrease of bulk contribution to transport in thinner films. As can be seen clearly in figure 3(b), the $R_{2D}$ value at $T = 300$ K increases from 0.6 kΩ for 30 QL to 4.4 kΩ for 5 QL.

The Seebeck coefficients of all the Bi$_2$Se$_3$ thin films (figure 2(b)) are negative, which is consistent with $n$-type bulk and surface charge carriers as revealed by the ARPES band maps. As expected for simple metals, the Seebeck

![Figure 3](image-url)
coefficients show a quasi-linear relationship with $T$ over the whole temperature range. With the decrease of film thickness, the general behavior of $S$ remains qualitatively the same but the absolute value $|S|$ decreases very systematically. Figure 3(a) summarizes the thickness dependence of $S$ measured at $T = 300$ K of the six Bi$_2$Se$_3$ films. The value of $S$ changes smoothly from $-104.3 \, \mu V \, K^{-1}$ for 30 QL to $-64.6 \, \mu V \, K^{-1}$ for 5 QL. As a consequence, the thermoelectric power factor $S^2\sigma$ shown in figure 2(c) drops significantly with reducing film thickness. Therefore, decreasing the film thickness, or lowering the dimensionality of the Bi$_2$Se$_3$ TI system, is actually detrimental to the thermoelectric performance.

To understand the experimental observations, we perform band structure and thermopower calculations for Bi$_2$Se$_3$ thin films with varied thicknesses. The existence of 2D Dirac-like surface bands within the insulating bulk gap is clearly visualized in figure 4(a) for 7 QL Bi$_2$Se$_3$. As the film thickness increases, the dispersion of surface bands remains essentially unchanged, but the number of bulk bands increases and their dispersion varies noticeably due to the quantum confinement effect. The thickness-dependent characteristics of the band structure is reflected in $M(E)$, which is proportional to the DOS times carrier velocity [21]. As shown in figure 4(b), $M(E)$ increases gradually with film thickness in the bulk-band region and becomes thickness independent in the bulk-gap region. A linear energy dependence of $M(E)$ starting from the Dirac point is clearly shown within the bulk gap, which is a hallmark of 2D surface states with linear dispersion.

We can also make more quantitative comparisons between theory and experiment. The calculated BCB minimum is 0.24, 0.26 and 0.15 eV above the Dirac point for 7, 10 and 20 QL Bi$_2$Se$_3$, in good agreement with the ARPES results. In our calculations of the Seebeck coefficient, the $E_F$ position was set to be 0.111, 0.025, 0.022 and 0.020 eV above the BCB minimum for 7, 10, 15 and 20 QL, respectively, as determined by the ARPES results. The MFP ratio $r_l$ as the only free parameter was determined by comparing the calculated $S$ as a function of temperature with the experimental data. We selected $r_l$ to be 1.0, 2.0, 1.6 and 2.8 for 7, 10, 15 and 20 QL, respectively. As demonstrated in figure 4(c), there is an excellent agreement between theory and experiment for $S$ over a wide range of temperatures.

In order to explain why $S$ becomes smaller in thinner Bi$_2$Se$_3$ films, we need to consider both the surface and bulk contribution to $S$. Specifically, the total Seebeck coefficient $S$ is a weighted contribution of the channels:
In summary, we observe a systematic reduction of the Seebeck coefficient as well as a remarkable decrease of thermoelectric power factor in Bi2Se3 TI thin film when the thickness is reduced from 30 QL to 5 QL. These results can be understood by the combined bulk and surface state contribution to the thermoelectric properties of TI. The main origin of the thickness dependent behavior is the increasing contribution of the Dirac-like topological surface state, whose linear dispersion is not optimal to the thermopower. Another factor is the change of E_F position with film thickness, which affects the bulk thermopower value and the relative contribution of the surface states.

This work sheds important new light on the thermoelectric properties of 3D TIs, which are so far the best room temperature thermoelectric materials. Contrary to previous theoretical proposals [2, 6, 11], our results show that simply lowering the dimensionality of 3D TIs is not an effective way to enhance the thermoelectric performance. This is due to the existence of Dirac-like topological surface states, which were discovered only a few years ago. In order to improve the thermoelectric performance of 3D TI, it is perhaps necessary to reduce or completely remove the topological surface states. Possible approaches include further decreasing the film thickness to gap the surface state, as well as an optimization of the E_F position. For future investigations, we plan to tune the band structure of TI thin films by doping or gating to see the effect of the gapped topological surface state and the band topology on the thermopower, aiming to gain a deeper understanding of the thermoelectric properties of TIs and the methods to further improve them.

Acknowledgments

This work was supported by the National Natural Science Foundation of China and the Ministry of Science and Technology of China. YX acknowledges support from Tsinghua University Initiative Scientific Research Program. The calculations were done on the ‘Explorer 100’ cluster system of Tsinghua University and on the ‘Tianhe-2’ of National Supercomputer Computer Center in Guangzhou. SCZ is supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under contract DE-AC02-76SF00515. We also acknowledge the support from ENN Energy Holdings Limited.

References

[1] DiSalvo F J 1999 Science 285 703
[2] Dresselhaus M S, Chen G, Tang M Y, Yang R G, Lee H, Wang D Z, Ren Z F, Fleurial J P and Gogna P 2007 Adv. Mater. 19 1043
[3] Bell L E 2008 Science 321 1457
[4] Snyder G J and Toberer E S 2008 Nat. Mater. 7 105
[5] Sootsman J R, Chung D Y and Kanatzidis M G 2009 Angew Chem. Int. Edit. 48 8616
[6] Hicks L D and Dresselhaus M S 1993 Phys. Rev. B 47 12727
[7] Hicks L D and Dresselhaus M S 1993 Phys. Rev. B 47 16631
[8] Zhang H, Liu C-X, Qi X-L, Dai X, Fang Z and Zhang S-C 2009 Nat. Phys. 5 438
[9] Xia Y et al 2009 Nat. Phys. 5 398
[10] Chen Y L et al 2009 Science 325 178
[11] Osterhage H, Goeth J, Harndou B, Gwozd P, Zierold R and Nielsch K 2014 Appl. Phys. Lett. 105 123117
[12] Zhang J S et al 2015 Phys. Rev. B 91 075431
[13] Hinsche N F et al 2015 Acs Nano 9 4406
[14] Heremans J P, Jovovic V, Toberer E S, Saramat A, Kurosaki K, Charoenphakdee A, Yamanaka S and Snyder G J 2008 Science 321 554
[15] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[16] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[17] Mostofi A A, Yates J R, Lee Y-S, Souza I, Vanderbilt D and Marzari N 2008 Comput. Phys. Commun. 178 685
[18] Marzari N and Vanderbilt D 1997 Phys. Rev. B 56 12847
[19] Souza I, Marzari N and Vanderbilt D 2001 Phys. Rev. B 65 035109
[20] Yates J R, Wang X, Vanderbilt D and Souza I 2007 Phys. Rev. B 75 195121
[21] Maassen J and Lundstrom M 2013 Appl. Phys. Lett. 102 093103
[22] Zou X L, Chen X B, Huang H Q, Xu Y and Duan W H 2015 Nanoscale 7 8776
[23] Xu Y, Wang J-S, Duan W, Gu B-L and Li B 2008 Phys. Rev. B 78 224303
[24] Xu Y, Li Z and Duan W 2014 Small 10 2182
[25] Liu M et al 2011 Phys. Rev. B 83 165440