Few-quintuple Bi$_2$Te$_3$ nanofilms as potential thermoelectric materials

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The thermoelectric transport properties of p-type Bi$_2$Te$_3$ nanofilms with various quintuple layers (QL) were systematically investigated based on ab initio electronic structure calculations and Boltzmann transport equations. Our results demonstrated that p-type few-quintuple Bi$_2$Te$_3$ nanofilms could exhibit high thermoelectric performance. It was found out that the 1QL Bi$_2$Te$_3$ nanofilm had the highest ZT value as compared with other nanofilms, which is mainly attributed to the significant enhancement of the density of states near the edge of the valence band resulting from the strong coupling between the top and bottom electronic states and the quantum confinement effect. The dependence of the thermoelectric transport properties on carrier concentration and temperature was also discussed in detail, which can be useful for searching high-efficiency few-quintuple Bi$_2$Te$_3$ thermoelectric nanofilms.

Thermoelectric materials have attracted intense interest due to their potential applications in cooling and power generation$^{1-5}$. The performance of thermoelectric devices depends on the dimensionless figure of merit, ZT, which is defined as

$$ZT = \frac{S^2\sigma T}{k_l + k_e},$$

where $S$ is the Seebeck coefficient, $T$ is the temperature, $\sigma$ is the electrical conductivity, $k_l$ is the lattice thermal conductivity and $k_e$ is the thermal conductivity of the electronic carriers. To achieve a high ZT, it requires maximizing the Seebeck coefficient and electrical conductivity but minimizing the thermal conductivity. In general, the thermal conductivity can be minimized by introducing nanostructures into the thermoelectric materials to increase phonon scattering$^{6-8}$, the Seebeck coefficient can be enhanced by quantum confinement effects$^{9,10}$, and the electrical conductivity can be improved by adjusting the carrier concentration through doping$^{11,12}$, however, the interdependence among these parameters makes the maximization of ZT a challenge so far.

Among various thermoelectric materials, Bi$_2$Te$_3$ and its solid solutions have been investigated intensely because they possess outstanding thermoelectric properties at room temperature, which is due to the high degeneracy at the edges of their energy bands. The ZT value of the Bi$_2$Te$_3$-based thermoelectric materials has been improved by many approaches such as the synthesis of nanostructured bulk materials or nanocomposites with a precise control of the size, structure, composition and carrier concentration as well as the deposition of various thin films by melt-spinning, sputtering, evaporation and molecular beam epitaxy$^{13-16}$. Recently, Bi$_2$Te$_3$ has been demonstrated as a three-dimensional (3D) topological insulator, which further stimulates a strong research interest in this material$^{17}$. Bulk Bi$_2$Te$_3$ crystallizes in a rhombohedral unit cell with the space group $D_{3d}^3$ ($R3m$) and has a layered structure with five atomic layers referred to as a quintuple layer (QL)$^{18,19}$. The interaction between two adjacent QL is of the weak van der Waals type, which allows one to disassemble Bi$_2$Te$_3$ crystal into its quintuple building block$^{20}$. The experimental results have shown that the exfoliated quintupiles and ultrathin few-quintuple films have a low thermal conductivity, which is favorable to improve the thermoelectric performance$^{20}$. Very recently, an efficient thermoelectric conversion was observed in the atomic monolayer steps of Bi$_2$Te$_3$ (n-type) and Sb$_2$Te$_3$ (p-type) QL by scanning photoinduced thermoelectric current probe$^{21}$. Theoretically, P. Ghaemi et al. have discovered that nanometer-scale Bi$_2$Te$_3$ thin film generates a hybridization-induced band gap of the unconventional surface states, which can lead to an increased thermoelectric performance at low temperatures$^{22}$. Recent theoretical researches show that Bi$_2$Te$_3$ nanofilms have enhanced thermoelectric properties$^{20,21}$. B. Qiu et al. have studied the thermal conductivity of the few-quintuple Bi$_2$Te$_3$ nanofilms by using molecular dynamics simulation and have shown that nanoporous Bi$_2$Te$_3$ nanofilms display significantly reduced...
thermoelectric transport coefficients. Previous calculations confirmed that it is an effective approach to predict the thermoelectric transport properties of bulk materials and nanosystems. By solving the Boltzmann transport equations, S and σ, can be obtained as:

\[ \sigma = A^{(0)} \]

\[ S = \frac{1}{eT} \left( \frac{A^{(1)}}{A^{(0)}} \right) \]

Computational methods

First-principles calculation. The calculation of the energy band structure has been performed by using the projector augmented wave (PAW) method within the framework of density functional theory and Boltzmann transport equations to provide a microscopic description of the thermoelectric properties of few-quintuple Bi₂Te₃ nanofilms. Our results demonstrate that p-type few-quintuple Bi₂Te₃ nanofilms can exhibit high thermoelectric performance and thus they can stand as a promising candidate for nanoscale thermoelectric applications.

Calculation of the transport properties. In this work, the semi-classical Boltzmann equations with the relaxation time approximation were used to evaluate the thermoelectric transport coefficients. Previous calculations confirmed that it is an effective approach to predict the thermoelectric transport properties of bulk materials and nanosystems. By solving the Boltzmann transport equations, S and σ, can be obtained as:

\[ \sigma = A^{(0)} \]

\[ S = \frac{1}{eT} \left( \frac{A^{(1)}}{A^{(0)}} \right) \]

Results and discussion

Band structure. The ab initio electronic band structures of Bi₂Te₃ bulk material and nanofilms with various thicknesses are shown in Fig. 2. The spin-orbit interaction was taken into account in the calculation, which was proved to be essential for calculating the electronic structures of Bi₂Te₃ and our results for bulk Bi₂Te₃ (Fig. 2(a)) are in good agreement with the data reported in previous work. As shown in Figs. 2(b–f), band structures of the Bi₂Te₃ nanofilms are similar to each other except for the significant difference in band gap and energy spacing between adjacent bands. Firstly, the indirect band gap decreases with increasing the film thickness. For example, the
The band gap is about 320 meV for 1QL film (Fig. 2(b)) and it disappears when the film thickness increases to 3QL (Fig. 2(d)). Secondly, the energy spacing between the adjacent bands decreases with increasing the number of QL. The reasons are that with the thickness increasing, the coupling between the top and bottom electronic states and the quantum confinement effect on the electrons in the nanofilm are weakened. It is also noteworthy to point out that the conduction bands of all five nanofilms are much more dispersive than the valence bands.

The density of states (DOS) for the Bi$_2$Te$_3$ nanofilms with various thicknesses is shown in Fig. 3. The DOS near the edge of the valence band has a sharper and larger peak than that near the edge of the conduction band due to flatter valence bands (as shown in Fig. 2). It can be observed from Fig. 3 that the total DOS for 1 QL Bi$_2$Te$_3$ nanofilm displays staircase-like behavior near the edges of conduction bands and valence bands, induced by the quantum confinement effect in quasi-2D systems. With the number of QL decreasing, the spacing between the peaks (singularity) of the DOS significantly increases, which is consistent with the change of the energy spacing between the adjacent bands.

**Transport properties.** Based on the calculated electronic band structures, the thermoelectric transport coefficients of the few-quintuple Bi$_2$Te$_3$ nanofilms can be evaluated by the methods presented in Sec. II. It is well known that the standard density functional theory usually underestimates the band gaps of semiconductors. In order to achieve a better agreement with the experimental results, the band gaps of the nanofilms were adjusted to match the experimental data by applying the so-called scissor operator in our calculations. Similar treatments have been widely adopted in previous publications.

Fig. 4 shows the calculated electrical conductivity, Seebeck coefficient, power factor and figure-of-merit of the perfect p-type Bi$_2$Te$_3$ films with different QL and p-type bulk Bi$_2$Te$_3$, as a function of carrier concentration at 300 K. As shown in Fig. 4(a), the electrical conductivity of all the p-type Bi$_2$Te$_3$ nanofilms increases with increasing carrier concentration. In contrast, the Seebeck coefficient decreases with increasing carrier concentration and in general the Seebeck coefficient for the thinner nanofilm is larger than that for the thicker nanofilm at the same carrier concentration (Fig. 4(b)). This can be explained by the following discussion. Taking into account that Maxwell-Boltzmann approximation is justified in the region of $E_F = E_V \gg k_B T$, $S$ can be expressed as a function of $n$:

$$S = -\frac{k_B}{e} \ln \left( \frac{n}{N_V} \right) + \frac{k_B}{e} A_V, \quad (8)$$

where $N_V$ is the effective density of states at the edge of the highest valence band and $A_V$ represents a scattering factor of the semiconductor. $N_V$ can be expressed as

$$N_V = \int_{-\infty}^{E_V} g_V(\varepsilon) \exp\left[-(E_V - \varepsilon)/k_B T\right] d\varepsilon, \quad (9)$$

where $g_V(\varepsilon)$ is the density of states. Eq. (8) directly reveals that the magnitude of $S$ decreases with increasing $n$, as shown in Fig. 4(b). In addition, with the number of QL decreasing, the DOS near the edge of the valence band increases due to the quantum confinement effect (Fig. 3), leading to an increase of $N_V$ and hence an enhancement of $S$. It is worth noting that $S$ of 1QL Bi$_2$Te$_3$ nanofilm is significantly larger than those of other nanofilms, which results from the significantly increased DOS near the edge of the valence band.
enhanced DOS near the edge of the valence band induced by the strong coupling between the top and bottom electronic states and the quantum confinement effect. The electrical conductivity $\sigma$ increases with increasing carrier concentration $n$, whereas the Seebeck coefficient $S$ decreases, therefore, there is an optimized carrier concentration, $n_{\text{opt}}$, at which the power factor is maximized (as shown in Fig. 4(c)). The $n_{\text{opt}}$ to obtain the maximum power factor for Bi$_2$Te$_3$ nanofilms with various QL occurs in the range from $0.3 \times 10^{20}$ cm$^{-3}$ to $5 \times 10^{20}$ cm$^{-3}$. In general, the $n_{\text{opt}}$ increases with decreasing the number of QL. The $n_{\text{opt}}$ can be derived as:

$$n_{\text{opt}} = N_V \exp(-2 + A_V).$$  

Eq. (10) reveals that the $n_{\text{opt}}$ for the power factor is proportional to $N_V$. With the number of QL decreasing, the DOS near the edge of the valence band increases, thus, $N_V$ rises and hence $n_{\text{opt}}$ increases (as shown in Fig. 4(c)). Figure 4(d) shows that the dependence of $ZT$ on the carrier concentration is similar to that of the power factor, indicating that the carrier concentration is a key parameter to adjust the thermoelectric performance of the few-quintuple films. The $n_{\text{opt}}$ to obtain the highest $ZT$ value is in the range from $0.1 \times 10^{20}$ cm$^{-3}$ to $1.5 \times 10^{20}$ cm$^{-3}$. The perfect 1QL film has the largest $ZT$ value of 1.0 at an $n_{\text{opt}}$ of $1.5 \times 10^{20}$ cm$^{-3}$. The $n_{\text{opt}}$ for the ZT is different from that for the power factor because of the effect of the electronic thermal conductivity that is related to the carrier concentration. We have calculated the thermoelectric transport properties of bulk Bi$_2$Te$_3$ by using the value of $2.2 \times 10^{-14}$ s at 300 K$^{22}$ for the relaxation time and the value of 1.5 W/mK at 300 K$^{36}$ for the phonon thermal conductivity. Our calculated results are in excellent agreement with the previous theoretical$^{32}$ and experimental data$^{36}$. It can be seen from Fig. 4 that the electrical conductivity of bulk Bi$_2$Te$_3$ is larger while the seebeck coefficient is smaller in most range of carrier concentrations, as compared with those of Bi$_2$Te$_3$ nanofilms at a fixed carrier concentration. The optimized $ZT$ value of bulk Bi$_2$Te$_3$ is about 0.6, which is smaller than that of 1QL Bi$_2$Te$_3$ nanofilm (Fig. 4(d)).

Fig. 5 shows the calculated electrical conductivity, Seebeck coefficient, power factor and figure of merit of the perfect 1QL Bi$_2$Te$_3$ nanofilm as a function of carrier concentration at different temperatures. As shown in Fig. 5(a), at a fixed carrier concentration the electrical conductivity decreases with increasing temperature, mainly because the scattering rate of the carriers increases and the relaxation time decreases with increasing temperature (as shown in Table 1). In contrast, the $S$ slightly increases with increasing the temperature at a fixed carrier concentration, as shown in Fig. 5(b). This is mainly because when the temperature rises, the term, $\exp(-\left(E_V - \varepsilon\right)/k_B T)$ with $\varepsilon < E_V$, in Eq. (9) increases and then it leads to an increasing $N_V$. Due to the reduction of $\sigma$, the power factor decreases with increasing temperature and the $n_{\text{opt}}$ to obtain the maximum power factor shifts to a larger value (Fig. 5(c)). Fig. 5(d) shows that the dependence of $ZT$ on the temperature is reversed as compared with that of the power factor. Although the power factor decreases with raising temperature, $ZT$ value increases because both phonon and electron thermal conductivity decrease. The peak values of $ZT$ for the p-type perfect 1QL Bi$_2$Te$_3$ film are 1.0 and 1.9 at 300 K and 800 K, respectively.

Figs. 6(a) and 6(b) summarize the dependence of the optimized $ZT$ (at $n_{\text{opt}}$) of the p-type perfect and nanoporous Bi$_2$Te$_3$ nanofilms with various QL on temperature, respectively. As shown in Fig. 6(a), for all of the perfect nanofilms, their optimized $ZT$ values increase with increasing temperature and 1QL nanofilm has the highest optimized $ZT$ value in the entire temperature range as compared with other nanofilms. The temperature dependence of optimized $ZT$ value has also been found in the previous study of thermoelectric properties of 1QL Bi$_2$Te$_3$ nanofilm$^{25}$. For the nanofilms with a thickness larger than 1QL, their $ZT$ values are close to each other because they possess approximately similar DOS near the edge of the valence band. Therefore, the molecular dynamics simulations showed that the phonon thermal conductivity can be significantly reduced by introducing structure defects such as nanopore$^{26}$. Considering the fact that phonon thermal conductivity can be significantly reduced by introducing defects without significantly sacrificing the thermoelectric power factor $S^2\sigma$,$^{18}$ which has
been seen as a main strategy to enhance the thermoelectric properties of materials and has been confirmed by a lot of experimental works. We give the calculated results of thermoelectric properties of nanoporous Bi$_2$Te$_3$ nanofilms by assuming that introduction of nanopores don’t influence the electronic structure and power factor of nanofilms. Due to the reduction of phonon thermal conductivity, the p-type Bi$_2$Te$_3$ nanofilms with nanopore defects exhibit a significantly improved $ZT$ value as compared with the perfect nanofilms. Particularly, the 1QL nanoporous Bi$_2$Te$_3$ nanofilms can achieve an optimized $ZT$ value of 2.65 at room temperature, as shown in Fig. 6(b). The temperature dependence of the optimized $ZT$ values of the p-type Bi$_2$Te$_3$ nanofilms with nanopore defects becomes complicated in comparison to that of the perfect nanofilms. This can be explained by the following discussions. By using the Wiedemann–Franz law: $\kappa_e = L\sigma T$, the $ZT$ may be written as follows:

$$ZT = \frac{S^2 L}{\kappa_e (1 + S/\kappa_e)}$$ \hspace{1cm} (11)

For perfect Bi$_2$Te$_3$ nanofilms, the phonon dominates thermal transport ($\kappa_l \gg \kappa_e$), and $ZT$ increases with temperature mainly due to that $\kappa_l$ decreases with temperature. For nanoporous Bi$_2$Te$_3$ nanofilms, $\kappa_l$ remains constant over the entire temperature range and $ZT$ depends on temperature through $S$ and $\kappa_e$ according to Eq. (11). In this case, the values of $\kappa_l$ and $\kappa_e$ at optimized carrier concentration are comparable to each other. The temperature dependence of the optimized $ZT$ values of nanoporous Bi$_2$Te$_3$ nanofilms is less prominent than that of perfect nanofilms, and several factors including $S$ and $\kappa_e$ as well as its magnitude relative to $\kappa_l$ come into effect. We hope that these predictions could provide a clue for experimental researchers to optimize the thermoelectric performance of Bi$_2$Te$_3$ nanofilms.

**Conclusions**

In summary, we have employed a combination of first-principles electronic structure and Boltzmann transport calculations to predict the thermoelectric transport properties of few-quintuple Bi$_2$Te$_3$ nanofilms. Our results show that p-type Bi$_2$Te$_3$ nanofilms could be good candidates for thermoelectric nanomaterials, provided that the phonon thermal conductivity can be decreased by introducing structure defects without significantly sacrificing the thermoelectric power factor, and p-type 1QL nanofilm with nanopore defects can...
achieve an upper-limit $ZT$ value of 2.65 at room temperature. It was found that the p-type 1QL Bi$_2$Te$_3$ nanofilm as compared with other nanofilms has the highest $ZT$ value, which is mainly attributed to the significantly enhanced density of states resulting from the strong coupling between the top and bottom electronic states and the quantum confinement effect. The dependence of thermoelectric transport properties on doping level and temperature was investigated in detail, which provides guidance for future experiments to optimize $ZT$ value of p-type Bi$_2$Te$_3$ nanofilms with few quintuple layers. The type of calculation reported in this work represents a valuable investigation tool to study the thermoelectric properties of quasi-2D nanomaterials.

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