Thermal conductivity prediction and analysis of few-quintuple Bi_2Te_3 thin films: A molecular dynamics study

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In this work, we use molecular dynamics simulations to predict the thermal conductivities of perfect and nanoporous few-quintuple Bi_2Te_3 thin films. We find the dimensional crossover behavior of thermal transport and a minimum thermal conductivity at three quintuple layers at room temperature, and we attribute it to the interplay between phonon Umklapp scattering and boundary scattering. Also, nanoporous films show significantly reduced thermal conductivity compared to perfect thin films, indicating that they can be very promising thermoelectric materials. © *2010 American Institute of Physics*. [doi:10.1063/1.3514252]

Bi_2Te_3 as well as its alloys have long been the best thermoelectric materials around room temperature. Among its derived nanostructures,[1–8] thin films have been synthesized and characterized extensively[1,4–8] for enhanced figure of merit *ZT* due to charge carrier confinements[9] and phonon confinements.[10] Recently, pioneering work has been done on the creation of Bi_2Te_3 films down to a few quintuple layers (QLs) using mechanical exfoliation,[4,5] and initial measurements on stacked few-QL thin films show significantly reduced thermal conductivity compared to the bulk phase.[5,11] However, besides the limited experimental data, theoretical studies of phonon transport are not available in few-quintuple Bi_2Te_3 thin films. For such quasi-two-dimensional (2D) systems, unusual thermal transport phenomena may arise, such as the dimensional crossover behavior seen in few-layer-graphene (FLG).[12] Also, Bi_2Te_3 has recently been identified as one of a new class of materials named topological insulators,[13] opening a completely new mechanism for Bi_2Te_3 nanostructures such as the few-quintuple Bi_2Te_3 thin films to be promising thermoelectric materials. In this letter, we use molecular dynamics (MD) simulations to predict and analyze the lattice thermal conductivity of few-quintuple Bi_2Te_3 perfect films and nanoporous films. We find interesting dependence of the thermal conductivity on the number of quintuples governed by the interplay of interquintuple (Umklapp) scattering and boundary scattering. Also the thermal conductivity of nanoporous thin films shows remarkable reduction compared to perfect films. Our results are useful in developing high-performance thermoelectric materials based on few-quintuple Bi_2Te_3 thin films.

The basic building block of Bi_2Te_3 crystal is a QL composed of five consecutive Te1–Bi–Te2–Bi–Te1 atomic layers bounded by partially-covalent bonds and electrostatic interactions.[14] Between QLs, the Te1–Te1 bonds possess mixed electrostatic and van der Waals nature, so that they can be easily separated to form single-quintuple or few-quintuple thin films.[4] Geometries of Bi_2Te_3 few-quintuple thin films used in this work are shown in Fig. 1, where nanoporous films with concentrated or distributed pores by removing 5% atoms from perfect films are also considered. In our MD simulations, the two-body interatomic potentials for Bi_2Te_3 developed in our previous work are employed.[14] Free boundary conditions are applied in the cross-plane direction for the finite film thickness while periodic boundary conditions are used for the other two directions to mimic infinitely large size. Simulation domain size effects have been checked in these systems and it is found that the thermal conductivity differs little with six or more unit cells in periodic directions. The simulation procedure is similar to that described in our previous work.[14] Verlet leapfrog algorithm is used with a timestep of 1.25 fs, and all simulations are 2.5 ns long. The system is first run in constant volume and temperature ensemble (NVT) for 250 ps and then switched to constant volume and energy ensemble (NVE) for another 250 ps. Heat current $S(t)$ is extracted from the last 2 ns in NVE and post-processed to obtain the heat current autocorrelation function (HCACF) $\langle S(t)S(0)\rangle$. Through appropriate Fourier filters, the HCACFs are fitted with exponential functions $G(t)$.[14] Then based on Green–Kubo formulism, the lattice thermal conductivity is obtained as

$$\kappa_L = \frac{1}{k_B V T^2}\int_0^\infty G(t)dt, \tag{1}$$

where k_B is the Boltzmann constant, V is the effective system volume, and T is the temperature. For each obtained thermal

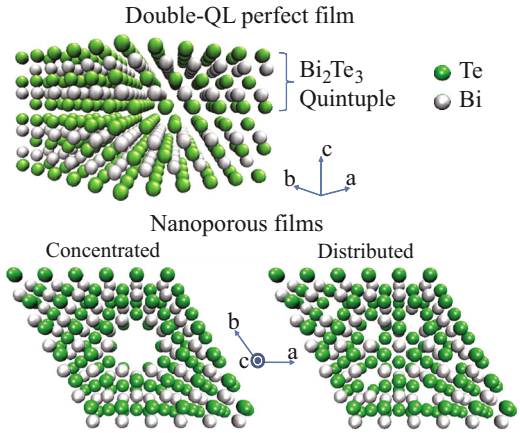

FIG. 1. (Color online) Geometries of Bi_2Te_3 thin films. Top: side view of double-QL perfect film. Bottom left: top view of nanoporous films with concentrated pores. Bottom right: top view of nanoporous films with distributed pores.

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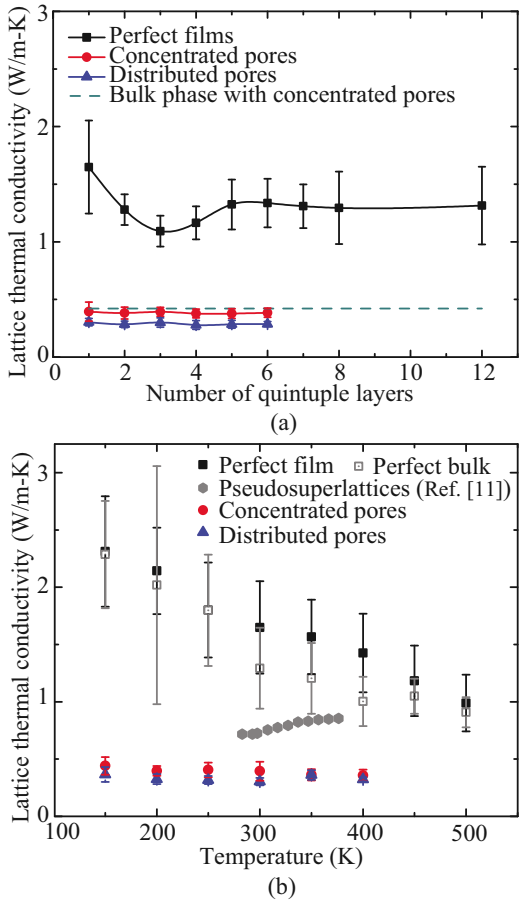

FIG. 2. (Color online) (a) The lattice thermal conductivity of perfect and nanoporous films at 300 K with respect to the number of QLs. (b) The lattice thermal conductivity of single QL perfect/nanoporous films along with bulk values (Ref. 14) and pseudosuperlattices values from Ref. 11 as a function of temperature.

conductivity data point, ten independent simulations are performed and averaged to minimize statistical fluctuations.

In Fig. 2(a), we show the lattice thermal conductivity of Bi_2Te_3 thin films at room temperature as a function of the number of QLs. When the number of QLs decreases from 12 to 3, the thermal conductivity decreases as expected from the classical size effect for thin films. Overall, the thermal conductivity in this region exhibits moderate reduction from the bulk value (1.3 W/m K) predicted with the same interatomic potentials in our previous work,[14] and these simulation results are consistent with the measured κ for stacked few-quintuple Bi_2Te_3 thin films where reduced thermal conductivity was seen.[4,5] Interestingly, the thermal conductivity bounces back when the number of QLs further reduces from 3 to 1, such that a minimum of κ of 1.1 W/m K is present at 3 QLs. The presence of a minimum thermal conductivity indicates a transition of thermal transport from three-dimensional to quasi-2D in few-quintuple Bi_2Te_3 films. Although such dimensional crossover has not been reported for Bi_2Te_3 thin films in experiments yet, similar behavior has been seen in FLG, as FLG with fewer layers having greater thermal conductivity.[12] However, no minimum thermal conductivity is seen there.[12] Such difference can be understood by considering the interplay between the Umklapp scattering and boundary scattering. When the number of layers increases, the suppressed out-of-plane transverse acoustic mode (ZA) mode contribution due to the enhanced Umklapp

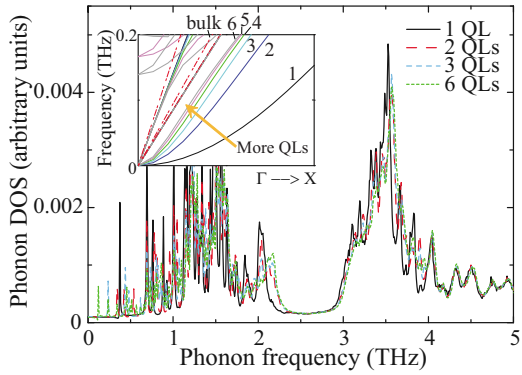

FIG. 3. (Color online) Phonon DOS of thin films of 1–6 QLs. Inset: The lowest 0.2 THz phonon dispersions along $\Gamma - X$ direction.

scattering rate tends to reduce κ as shown in Refs. 12 and 15, while the reduced boundary scattering rate tends to increase κ. Whether κ would eventually decrease or increase depends on which mechanism dominates. For Bi_2Te_3, the intrinsic phonon mean free path (MFP) is only several nanometer, such that the real space extension of coupling among phonon states is weak, the effect of increased Umklapp scattering due to layer stacking only dominates up to a few QLs. For more layers this mechanism diminishes while the boundary scattering effect starts to dominate. Therefore, a minimum in thermal conductivity is found at very few QLs. In contrast, FLG has a long intrinsic phonon MFP, such that the effect of increased Umklapp scattering due to layer stacking can act up to more layers and can always dominate over the effect of reduced boundary scattering. This gives a monotonically decreasing thermal conductivity with more layers for FLG as observed experimentally.[12]

In Fig. 2(b), the lattice thermal conductivities of the single-QL thin film and the bulk phase are shown as a function of temperature. The close to T^{-1} dependence indicates the Umklapp scattering to be the dominating phonon scattering mechanism. As a reference, we also show the measured temperature-dependent thermal conductivity of stacked few-quintuple films (pseudosuperlattice) reported in Ref. 11. These values are lower than our predicted values for individual films composed of single- or multiple-quintuples, since the mechanical stacking of multiple thin films can introduce additional phonon scattering channels due to interface, misalignment between films, roughness, defects, etc. The weak temperature dependence indicates a strong phonon-boundary scattering nature, consistent to the trend observed in our nanoporous films (to be discussed in detail later) which are also phonon-boundary dominant. Overall, our prediction results are well consistent with the experimental data reported in Ref. 11.

To gain more insight, the phonon density of states (DOS) and dispersions for thin films of 1–6 QLs are computed, as shown in Fig. 3. The DOS peaks (especially in low frequency acoustic branches) of single QL are narrow, consistent with the fact that there are fewer phonon states satisfying energy and momentum conservation for scattering in quasi-2D systems. For more QLs, the DOS peaks are generally broadened, indicating that more phonon states become available for Umklapp scattering. However, when the number of QLs goes beyond 3, the DOS almost collapse, suggesting that the enhancement in Umklapp scattering becomes less efficient with larger number of QLs. From the in-plane

phonon dispersion relations for frequencies below 0.2 THz (inset of Fig. 3), we find that all films have linear TA and longitudinal acoustic (LA) branches, as well as a quadratic ZA branch. For single QL, phonon boundary scattering is present in addition to Umklapp process, which can be inferred from the weaker temperature dependence of its thermal conductivity than that of bulk [Fig. 2(b)]. While stacking multiple QLs has little effect on TA and LA modes, it hardens the ZA mode and increases the group velocity. When more QLs are stacked, the change in boundary scattering at thin film surfaces dominates over the change in Umklapp process, and the classical size effect gradually emerges, leading to the minimum at 3 QLs.

We also simulated nanoporous thin films and found significant reduction in thermal conductivity as compared to bulk, as shown in Figs. 2(a) and 2(b), indicating that they can be very promising thermoelectric materials. The thermal conductivity is only weakly temperature dependent and stays almost as a constant from single to many QLs and to bulk with values below 0.5 W/m K. This indicates that at 5% porosity the pore scattering dominates all other scattering mechanisms. Furthermore, at the same porosity, films with distributed pores show lower thermal conductivity due to multiple scattering at distributed pores.

In summary, we have used MD simulations to predict the thermal conductivities of perfect and nanoporous few-quintuple Bi_2Te_3 thin films. The findings of the dimensional crossover of thermal transport and a minimum thermal conductivity in perfect thin films are attributed to the interplay between phonon Umklapp scattering and boundary scattering. Thin films with nanosized pores show low and weakly temperature-dependent thermal conductivity due to strong pore scattering.

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[1]R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, Nature (London) **413**, 597 (2001).
[2]B. Poudel, Q. Hao, Y. Ma, Y. Lan, A. Minnich, B. Yu, X. Yan, D. Wang, A. Muto, D. Vashaee, X. Chen, J. Liu, M. S. Dresselhaus, G. Chen, and Z. Ren, Science **320**, 634 (2008).
[3]A. Mavrokefalos, A. L. Moore, M. T. Pettes, L. Shi, W. Wang, and X. Li, J. Appl. Phys. **105**, 104318 (2009).
[4]D. Teweldebrhan, V. Goyal, M. Rahman, and A. A. Balandin, Appl. Phys. Lett. **96**, 053107 (2010).
[5]D. Teweldebrhan, V. Goyal, and A. A. Balandin, Nano Lett. **10**, 1209 (2010).
[6]C. Chen, Y. Chen, S. Lin, J. C. Ho, P. Lee, C. Chen, and S. R. Harutyunyan, J. Phys. Chem. C **114**, 3385 (2010).
[7]M. Takashiri, M. Takiishi, S. Tanaka, K. Miyazaki, and H. Tsukamoto, J. Appl. Phys. **101**, 074301 (2007).
[8]D. Kim, E. Byon, G. Lee, and S. Cho, Thin Solid Films **510**, 148 (2006).
[9]M. Dresselhaus, G. Dresselhaus, X. Sun, Z. Zhang, S. Cronin, and T. Koga, Phys. Solid State **41**, 679 (1999).
[10]A. Balandin and K. L. Wang, J. Appl. Phys. **84**, 6149 (1998).
[11]V. Goyal, D. Teweldebrhan, and A. A. Balandin, Appl. Phys. Lett. **97**, 133117 (2010).
[12]S. Ghosh, W. Bao, D. L. Nika, S. Subrina, E. P. Pokatilov, C. N. Lau, and A. A. Balandin, Nature Mater. **9**, 555 (2010).
[13]Y. L. Chen, J. G. Analytis, J. H. Chu, Z. K. Liu, S. K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z. X. Shen, Science **325**, 178 (2009).
[14]B. Qiu and X. Ruan, Phys. Rev. B **80**, 165203 (2009).
[15]J. H. Seol, I. Jo, A. L. Moore, L. Lindsay, Z. H. Aitken, M. T. Pettes, X. Li, Z. Yao, R. Huang, D. Broido, N. Mingo, R. S. Ruoff, and L. Shi, Science **328**, 213 (2010).