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Enhanced thermoelectric performance of nanostructured topological insulator Bi₂Se₃

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To enhance thermoelectric performance by utilizing topological properties of topological insulators has attracted increasing attention. Here, we show that as grain size decreases from microns to ~80 nm in thickness, the electron mobility μ increases steeply from 12–15 cm²V⁻¹s⁻¹ to ~600 cm²V⁻¹s⁻¹, owing to the contribution of increased topologically protected conducting surfaces. Simultaneously, its lattice thermal conductivity is lowered by ~30%–50% due to enhanced phonon scattering from the increased grain boundaries. As a result, thermoelectric figure of merit, ZT, of all the fine-grained samples is improved. Specifically, a maximum value of ZT = ~0.63 is achieved for Bi₂Se₃ at T = ~570 K.

Thermoelectric materials have attracted tremendous attention for their ability to convert energies between heat and electricity directly. The efficiency of thermoelectric materials can be characterized by the dimensionless thermoelectric figure of merit ZT = S²σ/k, where S, σ, k, and T are the thermopower, electrical conductivity, thermal conductivity, and the absolute temperature, respectively. As we know, Bi₂Se₃ is an important constituent alloy in the state-of-the-art n-type thermoelectric material (Bi₂Te₃)₁₋ₓ(Bi₂Se₃)ₓ (typically with x = ~0.1, i.e., Bi₂Te₂.7Se₀.₃) operating at near room temperatures. However, so far one has paid much less attention to investigations on the thermoelectric properties of Bi₂Se₃ itself. Up to now, the reported maximum value of ZT in pristine Bi₂Se₃ is not higher than 0.35. Nonetheless, the potential thermoelectric performance of Bi₂Se₃ could be far more than the best value one has obtained so far, as is shown theoretically by Parker and Singh.⁶

On the other hand, recently Bi₂Se₃ is proven to be a three-dimensional topological insulator (3DTI) that has a robust topological protected surface state even up to room temperature. This new quantum state of matter is characterized by gapped insulating bulk states and gapless conducting surface states (for 3DTI) that are not affected by non-magnetic defects. Very recently, 3DTIs have been theoretically proposed as good thermoelectric materials. The results showed that by utilizing the unique properties of TIs, i.e., topologically protected conducting surface states, the thermoelectric efficiency of TI materials can be markedly improved. Especially, Tretiakov et al. theoretically proposed an approach to increase thermoelectric efficiency by nano-structuring the 3D topological insulators and showed that ZT can be much higher than unity. Although one has difficulties in realizing the holey structure experimentally as they proposed, the concept of increasing the surface to bulk ratio to increase the contribution of conducting surfaces of 3DTIs is illuminating to the improvement of their thermoelectric performance.

Here, we employed the approach of decreasing the grain size of bulk Bi₂Se₃ to nanometer scale to increase the surface to bulk ratio, whose effect is threefold (a schematic drawing of a 3DTI Bi₂Se₃ crystal with high conducting surfaces is depicted in Fig. 1): (1) to increase mobility (or electrical conductivity) due to an increased contribution of conducting surfaces, one of the key factor affecting the ZT; (2) to suppress lattice thermal conductivity through enhanced phonon scattering of the numerous interfaces (or grain boundaries, GBs); and (3) to increase thermopower through energy filtering effect due to carrier scattering at the interface potentials. Our results show that a high value of ZT = ~0.60 is obtained for the Bi₂Se₃ samples at T > 450 K due to increased contribution of conduction surfaces upon decreasing grain dimensions.

The nanostructured Bi₂Se₃ samples were fabricated by hot pressing of the milled powders of the ingots obtained by melting method. The phase compositions of the hot pressed bulk samples were checked by X-ray diffraction (XRD) (see Fig. S1). One can see that all the diffraction patterns can be indexed to rhombohedral Bi₂Se₃, in good agreement with the structures. Additionally, the lattice parameters of the samples are consistent with the XRD data.

FIG. 1. A schematic drawing of a crystal for 3D topological insulator Bi₂Se₃. Therein, L is length (or transverse dimension) and d is the thickness (or longitudinal dimension) of the crystal, and δ (~3QL) is layer thickness of the conducting surfaces of the 3DTI.

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TABLE I. A list of milling time \( t_m \), orientation factor \( \gamma \), relative density \( D \), Hall coefficient \( R_H \), carrier concentration \( n \), and scattering factor \( \lambda \) for Bi\(_2\)Se\(_3\) samples.

<table>
<thead>
<tr>
<th>#</th>
<th>( t_m ) (min)</th>
<th>( \gamma )</th>
<th>( D ) (10(^3) g cm(^{-3}))</th>
<th>( R_H ) (10(^{-8}) (\Omega) m T(^{-1}))</th>
<th>( n ) (10(^{12}) m(^{-3}))</th>
<th>( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1#</td>
<td>10</td>
<td>0.33</td>
<td>7.14</td>
<td>41.84</td>
<td>1.49</td>
<td>0.53</td>
</tr>
<tr>
<td>S2#</td>
<td>20</td>
<td>0.46</td>
<td>7.30</td>
<td>49.52</td>
<td>1.26</td>
<td>0.03</td>
</tr>
<tr>
<td>S3#</td>
<td>30</td>
<td>0.18</td>
<td>7.08</td>
<td>7.93</td>
<td>7.88</td>
<td>0.47</td>
</tr>
<tr>
<td>S4#</td>
<td>40</td>
<td>0.15</td>
<td>7.09</td>
<td>7.65</td>
<td>8.17</td>
<td>0.32</td>
</tr>
<tr>
<td>S5#</td>
<td>50</td>
<td>0.16</td>
<td>7.16</td>
<td>7.32</td>
<td>8.54</td>
<td>0.28</td>
</tr>
</tbody>
</table>

\( \gamma \) is the number of sample.

\( b_m \) is milling time.

\( \gamma \) is orientation factor.

\( D \) is relative density.

\( R_H \) is Hall coefficient.

\( n \) is carrier concentration.

\( \lambda \) is scattering factor.

JCPDS card 00–033-0214. However, one notices that the intensity of (001) diffraction peaks for all the samples increases as compared with that of (001) peaks in the JCPDS card, indicating that all of the samples have the preferred orientation due to flake-like grains (also see Fig. S2) parallel to [001]. Quantitatively, the preferred orientation can be described by an orientation factor, defined as

\[
\gamma = \frac{P - P_0}{1 - P_0},
\]

where \( P \) is the fractional intensity of the (001) planes, \( P_0 \) is the value of \( P \) in the case of ideal isotropy, and \( P = \sum l(001)/\sum l(hk0) \). The calculated \( \gamma \) for each sample is listed in Table I. One can see that basically the value of \( \gamma \) decreases with increasing milling time \( t_m \), indicating that the sample anisotropy decreases with \( t_m \).

The field emission scanning electron microscopy (FESEM) images show that Bi\(_2\)Se\(_3\) samples have the thin and flake-like grains with the average dimensions that decrease with increasing \( t_m \) (Fig. S2). Thus, statistical grain dimensions in respective samples are shown in Fig. 2. One can see that whether the length (or transverse dimension) \( L \) or thickness (longitudinal dimension) \( d \) of Bi\(_2\)Se\(_3\) grains decreases monotonically with increasing \( t_m \). Specifically, the mean thickness \( d \) decreases from \(~330\) nm for \( t_m = 10\) min (S1\#) to \(~30\) nm for \( t_m = 50\) min (S5\#). (The equivalent grain dimension \( d_e \) is defined by the side-length of a cube with the same volume as the corresponding flake-like grain, as given in Fig. 2.) This reduction in the grain dimensions is also reflected by broadening of the diffraction peaks in the XRD patterns (see Fig. S1). If we assume the thickness of the gapless conducting surfaces \( \delta = 4.5\) nm (\(~3QL\)), the surface to bulk ratio \( f \) increases almost linearly from 4.5% to 42.7% as \( t_m \) increases from 10 min to 50 min, as shown in the inset of Fig. 2.

Fig. 3(a) shows that the resistivity \( \rho \) of samples S1\# and S2\# decreases monotonically with increasing temperature, exhibiting non-degenerate behavior. In contrast, \( \rho \) of samples S3\#, S4\#, and S5\# increases monotonically with increasing temperature, showing degenerate behavior. Specially, with decreasing grain dimensions \( \rho \) of Bi\(_2\)Se\(_3\) decreases remarkably. For instance, at \(~300\) K, \( \rho \) decreases from 2.6 \times 10\(^{-3}\) \(\Omega\)m for S1\# to 3.4 \times 10\(^{-5}\) \(\Omega\)m for S2\#, then it drops sharply to 1.2–1.6 \times 10\(^{-2}\) \(\Omega\)m for S3\#, S4\#, and S5\#.

Fig. 3(b) shows values of thermopower \( S \) for all the samples is negative, indicating they are n-type semiconductor. The absolute value of thermopower \( |S| \) of samples S1\# and S2\# basically decreases with increasing temperature, reflecting their non-degenerate behavior, in agreement with the temperature behavior of \( \rho \); while \( |S| \) of S3\#, S4\#, and S5\# increases basically with increasing temperature, manifesting degenerate behavior, being consistent with their \( \rho \sim T \) behavior (Fig. 3(a)). In addition, one notices that \( |S| \) decreases notably with decreasing grain dimensions. The measurements of Hall coefficient indicate that electron concentrations \( n \) basically increases with \( t_m \). For instance, \( n \) increases from 1.49 \times 10\(^{24}\) m\(^{-3}\) to 7.90 \times 10\(^{24}\) m\(^{-3}\) and finally to 8.54 \times 10\(^{24}\) m\(^{-3}\) as \( t_m \) increases from 10 min to 30 min and then 50 min (see Table I). This increase in \( n \) would result from the increased vacancies and anti-sites defects or dangling bands in (or near) GBs. Based on the data of \( \rho \) and \( n \) mobility \( \mu \) can be estimated, as shown in Fig. 3(c) that indicates that \( \mu \) increases from 12 to 15 cm\(^2\) V\(^{-1}\) s\(^{-1}\) as \( d \) decreases from 330 nm to 100 nm; then \( \mu \) increases steeply to \(~600\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) as \( d \) decreases to \(~80\) nm (or \( d_e = 120\) nm and \( f = 24% \)). As \( d \) decreases further, \( \mu \) decreases slightly. Usually, the mobility for conventional semiconductors or conductors always decreases with decreasing grain sizes due to enhanced carrier scattering by increased...
GBs, which is totally contradictory to the phenomenon observed here. Hence, one can reasonably attribute this steep increase in $\mu$ to the 3DTI properties of Bi$_2$Se$_3$, for as grain dimensions decrease, the volume fraction of the gapless conducting surfaces increases, through which larger proportion of electrons can transport, enhancing the overall mobility.

Hence, the decrease in $\rho$ with decreasing grain dimensions results from both increased $\mu$ and $n$. In addition, the decrease of $|S|$ with decreasing grain dimensions can mainly be ascribed to the increase in $n$. However, $S$ can also be enhanced by scattering at the potentials of GBs, as reflected by increases of scattering parameter $\lambda$.

Based on the experimental data of $n$ and $S$ and by using a single parabolic band model, $\lambda$ can be calculated as following:

$$m_d^* = \frac{\hbar^2}{2k_BT} \left( \frac{n}{4\pi F(1/\xi_{p,F})} \right)^{2/3},$$

with the Fermi integral of order $i$

$$F_i(x) = \int_0^\infty \frac{x^i}{1 + e^{x-\xi}} \, dx,$$

where $m_d^*$, $\hbar$, $\xi_F$, and $k_B$ are density state effective mass, Planck constant, the reduced Fermi level $E_F/(k_BT)$, and Boltzmann constant, respectively. In our estimation, we use $m_d^* = 0.16m_e$ (which is consistent with literature values) and assume acoustic phonon scattering ($\lambda = 0$) for coarse-grained Bi$_2$Se$_3$ sample (S1#). Then, the calculated $\lambda$ for fine-grained samples is obviously larger than zero and the largest value reaches 0.47 (see Table I), indicating that energy filtering effect occurs therein. The inset in Fig. 3(b) shows the Pisarenko relation (solid line) for S1# and the S values (at 300 K) for all the other samples, which indicates that S of the fine-grained Bi$_2$Se$_3$ samples (S3#, S4#, and S5#) enhanced obviously due to the energy-dependent scattering of electrons at the potentials of GBs.

Fig. 3(d) gives power factor PF ($= S^2/\rho$) for all the samples, which indicates that PF changes with grain dimensions non-monotonically and sample S2# has the largest PF with a peak value reaching ~15 $\mu$W cm$^{-1}$ K$^{-2}$ (~420 K) due to its higher $|S|$ value and relative low $\rho$.

Total thermal conductivity $\kappa$ of the samples is given in Fig. 4(a), which shows that $\kappa$ of S1# ranges from 1.5 W m$^{-1}$ K$^{-1}$ to 1.6 W m$^{-1}$ K$^{-1}$ at the investigated temperatures. With decreasing grain dimensions, $\kappa$ decreases almost monotonically. $\kappa$ for S5# has 0.6–0.8 W m$^{-1}$ K$^{-1}$, around 2.5 times smaller than that of S1#. Lattice thermal conductivity $\kappa_L$ can be obtained based on the relation: $\kappa = \kappa_L + \kappa_\kappa$, in which $\kappa_\kappa$ is the carrier contribution, which can be estimated by using the Wiedemann-Franz law: $\kappa_L = \text{LT}/\rho$, where L is the Lorenz number. Here, L $= 1.5 \times 10^{-8} \text{V}^2 \text{K}^{-2}$ is used, which is widely used in low-dimensional materials and non-degenerate semiconductors. As shown in the inset of Fig. 4(a), $\kappa_L$ decreases monotonically with decreasing grain dimensions. For instance, the lattice thermal conductivity $\kappa_L$ decreases from ~1.35 W m$^{-1}$ K$^{-1}$ (at 300 K) for S1# to 0.53 W m$^{-1}$ K$^{-1}$ (at 300 K) for S5#. This decrease in $\kappa_L$ can be attributed to the enhanced phonon scattering by GBs.

Fig. 4(b) shows ZT for all the samples, which indicates that ZT of all the fine-grained samples is larger than that of S1# in the whole temperature range studied here. At T $< 650 \text{ K}$, ZT of S2# is the largest, which increase from 0.60 to 0.63 as T increases from 450 K to ~570 K; then ZT of S2# declines with further increasing T. In contrast, ZT of S5# is larger than that of S3# and S4# and increase monotonically with increasing T; as a result, it surpass that of S2# at T $> 650 \text{ K}$, reaching ~0.60 at 670 K. Notably, the maximum ZT value ($\sim 0.63$) obtained here is substantially larger than all the reported values (ZT $\sim 0.096$–0.35) for Bi$_2$Se$_3$.

In summary, our study shows that as grain size of 3D topological insulators Bi$_2$Se$_3$ decreases from microns to ~80 nm in thickness, the electron mobility $\mu$ increases by 50 times at 300 K and $\kappa_L$ is lowered by ~30%–50%, owing to the enhanced contribution of topologically protected conducting surfaces. As a result, a largest value of ZT $\sim 0.60$–0.63 is obtained for the Bi$_2$Se$_3$ samples due to enhancement in both carrier mobility and phonon blocking simultaneously. Present results suggest that thermoelectric performance Bi$_2$Se$_3$ can be elevated substantially by utilizations of its gapless conducting surface.

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