A hybridized graphene carrier highway for enhanced thermoelectric power generation†

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Received 1st June 2012, Accepted 21st August 2012
DOI: 10.1039/c2cp42936e

The decoupling and enhancement of both Seebeck coefficient and electrical conductivity were achieved by constructing the c-axis preferentially oriented nanoscale Sb2Te3 film on monolayer graphene. The external graphene layer provided a highway for charge carriers, which were stored in the thicker binary telluride film, due to the extremely high mobility.

The global energy and environmental crisis makes the direct conversion of thermal energy to electricity based on the thermoelectric effect promising for waste heat recovery and non-polluting refrigeration systems.1–5 The efficiency of thermoelectric materials depends on the dimensionless thermoelectric figure-of-merit $zT = T^2S^2σ/k$ where $T$, $σ$ and $k$ are the Seebeck coefficient, absolute temperature, electrical conductivity and thermal conductivity, respectively. The realization of a high $zT$ is mainly due to the reduction in $k$ by creating nanostructure-engineered materials with dramatically increased phonon boundary scattering at interfaces.1,2 However, the thermoelectric power factor ($x^2σ$) has not yet improved much.1,3–5,6,7 Alternating layers of different materials in advanced superlattice structures demonstrated how $k$ can be reduced to near the theoretical minimum limit (0.2–0.5 W m$^{-1}$ K$^{-1}$).2,8

The reduction in $k$ alone may be sufficient to reach $zT$ values of up to 2, however the power factor also needs to be increased significantly to enhance $zT$ beyond 3.1,9

By far the most widely used thermoelectric materials for near-room temperature applications are binary telluride alloys with rhombohedral structures, such as Bi2Te3 (n-type) and Sb2Te3 (p-type), whose peak $zT$ values range between 0.8 and 1.1 with high $z$ and low $k$ values.2,10 These narrow band-gap semiconducting materials provide large $z$ since the charge carriers excited from the dopant level to conduction band have a greater average energy per carrier than that ($≈ k_BT$) of metals,11,12 where $k_B$ is the Boltzmann constant. There has also been an increased interest in the thermoelectric property of graphene, a hexagonal monolayer network of sp$^2$-hybridized carbon atoms. Although theoretical works on zigzag graphene nanoribbons suggested $zT$ as high as $≈ 4$ at room temperature, experimental works on graphene have demonstrated poor thermoelectric performance due to the low $z$, typically in the range of 30–100 μV K$^{-1}$, and high $k$.13–16 Structural defects have been utilized to overcome these hurdles. The phonon transmission might be significantly decreased,16 and the high-temperature $z$ of few-layer graphene could be enhanced by opening a band gap.13

Here we designed a phonon-glass electron-crystal heterostructure bilayer to decouple and independently optimize thermoelectric parameters. A c-axis preferentially oriented nanoscale binary telluride film, Bi2Te3 (n-type) or Sb2Te3 (p-type), was constructed on monolayer graphene. A higher concentration of carriers was stored in the thicker binary telluride layer with low $k$ (phonon-glass), and the graphene with high carrier mobility provided an electron-crystal structure. Fig. 1a shows the schematic of a specimen. The 4-point probe method was used to measure $σ$, and two probes were used to measure $x$. All the probes were placed on the top layer for the measurement of in-plane properties. The top binary telluride layer did not cover the entire surface of graphene to measure the contact resistance between two layers as will be discussed later. The experimental setup with probe configurations, calibration of thermocouples and Seebeck measurement devices, and acronyms of synthesized specimens are provided in Fig. S1–S3 and Table S1 (ESI†).

The thermoelectric properties of the monolayer graphene and pure Sb2Te3 film showed a
good agreement with those in the literature demonstrating reliability of the measurement techniques (Table S2 and S3, ESI).

As shown in Fig. 1b, monolayer graphene was synthesized on a copper foil by atmospheric pressure chemical vapor deposition and transferred onto a Si–SiO₂ substrate by the poly(methyl methacrylate) (PMMA)-assisted wet transfer method (see ESI for details). The Raman spectrum shows a high crystalline quality with pronounced 2D but negligible D modes. The transmittance of the graphene transferred onto a PET film was about 98% confirming the successful synthesis of monolayer graphene (Fig. 1b, inset). A thin binary telluride film was sputter-deposited on the transferred graphene on the Si–SiO₂ substrate (Fig. S4, ESI). The detailed synthesis procedures are described in ESI.

X-ray crystallographic analysis of sputtered Bi₂Te₃ films on the transferred graphene and bare Si–SiO₂ substrates (control) is shown in Fig. 1c. The diffraction peaks corresponding to the (00l) planes (c-axis preferential orientation perpendicular to the substrate surface) are typically enhanced when the substrate is heated during the molecular deposition process such as sputtering or evaporation. A thin binary telluride film was sputter-deposited on the transferred graphene on the Si–SiO₂ substrate (Fig. S4, ESI). The detailed synthesis procedures are described in ESI.

The unique structural anisotropy of the (00l) oriented Bi₂Te₃ film leads to enhanced σ and α while k is reduced by phonon scattering at interfaces between layers. A variety of methods have been investigated to synthesize binary telluride films with c-axis orientation including magnetron co-sputtering, molecular beam epitaxy and metal organic chemical vapor deposition. The dramatic enhancement of c-axis orientation of the deposited film on monolayer graphene by the simple sputtering method might open up an active area of research employing graphene as a synthesis scaffold. The enhancement of c-axis preferential orientation of the sputtered Sb₂Te₃ film on graphene was also observed (Fig. 1d). This structural anisotropy was maintained even when the film thickness was increased to 20 nm with a high Sb₂Te₃/graphene thickness ratio of ~60 (Fig. S5, ESI). The c-axis oriented growth of ZnO nanorods with a hexagonal crystal structure on the hexagonal basal plane of graphene in a low temperature solution process was recently reported. The surface topography of the c-axis oriented rhombohedral Sb₂Te₃ or Bi₂Te₃ is also composed of hexagonal crystals. Therefore, it is possible that graphene enhanced the preferential growth of the c-axis oriented binary telluride film due to the hexagonal lattice structure although the precise mechanism needs to be investigated further. As shown in Fig. 1e, graphene did not show any prominent mode around 1300 cm⁻¹ whereas the
D mode was significantly increased for GRP–Sb\(_2\)Te\(_3\) 10 nm after the sputtering process. The typical energy of sputter-depositing molecules is 10–100 eV\(^2\) which may induce structural disorder in graphene. The defects in graphene scatter electron transport and therefore decrease \(a\) as discussed in Fig. 2b. The defects also decrease \(k_l\) significantly.\(^{14}\)

Fig. 2a compares \(a\) of heterostructure bilayer films with those of single layers. The measurement was carried out multiple times for each sample, and the average and standard deviations are shown in Fig. 2a. The thermoelectric voltage and temperature difference of 3 different GRP–Sb\(_2\)Te\(_3\) 10 nm specimens are also provided in Fig. S6 (ESI\(^+\)). The standard deviations demonstrate the measurement uncertainty originated from the complexity and difficulty in measuring thermoelectric properties of thin films.\(^2\) The probe perturbation or the limited thermocouple resolution for the measurement of precise temperature difference may contribute to the possible error. A non-contact temperature measurement system with a finer resolution may improve the accuracy of measurements in the future. The thermoelectric effect of the Si–SiO\(_2\) substrate, used in all specimens, was not taken into account since it has negligible \(a\) and \(s\). The \(a\) of GRP, Sb\(_2\)Te\(_3\) 10 nm and Bi\(_2\)Te\(_3\) 10 nm were 63, 234 and 132 mVK\(^{-1}\)m\(^{-1}\), respectively, similar to the previously reported values for graphene and binary telluride films with high crystallinity.\(^{10,13,14,22,23,25,29}\) N-type materials exhibit negative \(a\) since the average energy of negative-charge electrons contributing to charge transport is greater than the Fermi energy whereas p-type materials show positive \(a\). The \(a\) of GRP–Sb\(_2\)Te\(_3\) 10 nm was 324 mVK\(^{-1}\)m\(^{-1}\) which was enhanced by 38 and 413% compared with those of Sb\(_2\)Te\(_3\) 10 nm and GRP, respectively. The \(a\) of GRP–Bi\(_2\)Te\(_3\) 10 nm was even smaller than that of Bi\(_2\)Te\(_3\) 10 nm. The construction of the n-type film (Bi\(_2\)Te\(_3\)) on the p-type substrate (graphene) induced the concomitant movement of both charge carriers along the temperature gradient, compensating carriers and subsequently cancelling out the resulting Seebeck voltage.\(^2\)
The precise mechanism for the enhancement of \( \alpha \) needs to be investigated further. It is possible that the \( \alpha \)-axis orientation of the Sb\(_2\)Te\(_3\) film on graphene contributed to increase in \( \alpha \). The increase in \( \alpha \) with the enhanced \( \alpha \)-axis orientation of telluride films was also previously reported in the literature.\(^{22,31}\)

Fig. 2b shows the electrical transport characteristics of GRP, Sb\(_2\)Te\(_3\) 10 nm, and GRP-Sb\(_2\)Te\(_3\) 10 nm. The sheet carrier density, Hall mobility and electrical conductivity of GRP were 2.07 \( \times \) 10\(^{12}\) cm\(^{-2}\), 2340 cm\(^2\) V\(^{-1}\) s\(^{-1}\), and 23 164 S cm\(^{-1}\), respectively. After the sputter deposition of Sb\(_2\)Te\(_3\) on graphene, there was a sharp increase in the D mode of Raman spectrum (Fig. 1e) and the mobility of GRP-Sb\(_2\)Te\(_3\) 10 nm was decreased compared with that of graphene (Fig. 2b). Compared with Sb\(_2\)Te\(_3\) 10 nm, the sheet carrier density of GRP-Sb\(_2\)Te\(_3\) 10 nm was much smaller which would increase \( \alpha \) (eqn S2, ESI\(^+\)) but decrease \( \sigma \) (eqn S3, ESI\(^+\)). It is likely that the different structures in the telluride films deposited on different substrates yielded different carrier concentrations although the precise mechanism between the telluride structure and carrier concentration needs to be investigated further. The decrease in the carrier density was overcome by the significantly greater mobility to achieve high \( \sigma \). Consequently, the conjugation of graphene to Sb\(_2\)Te\(_3\) increased \( \sigma \) by 87% compared with that of Sb\(_2\)Te\(_3\) 10 nm. The contact between the Sb\(_2\)Te\(_3\) and graphene layers was nearly Ohmic with a barrier height of 8.6 meV (Fig. S7, ESI\(^+\)), which is favorable for the diffusion of the higher concentration of thermally excited charge carriers in the thicker binary telluride film across the heterointerface and acceleration along the graphene with a significantly higher mobility. A simple 2-dimensional finite element analysis of Sb\(_2\)Te\(_3\) 10 nm and GRP-Sb\(_2\)Te\(_3\) 10 nm was also carried out using COMSOL 3.5a. Although this simple 2-dimensional continuum model does not reflect all the complicated physics of nanoscale bilayer films, it clearly demonstrates that the graphene layer can work as an inhomogeneous, high conductivity channel for carriers (see Fig. S8 for details, ESI\(^+\)).

As shown in Fig. 2c, the conflicting nature of \( \alpha \) and \( \sigma \) can be demonstrated using the simple theoretical model based on Boltzmann statistics, Jonker plot (\( \alpha - \ln \sigma \)),\(^{32,33}\) The data obtained in this study and control data from the literature are shown in solid stars and open symbols, respectively. For p-type semiconductors,

\[
\alpha = m(b - \ln \sigma) \quad (1)
\]

\[
m = k_B/e = 86.14 \mu V K^{-1} \quad b = A + \ln N_e \quad e \quad (2)
\]

where \( e \) is the charge of electron, \( A \) is the transport constant, \( N_e \) is the valence band DOS and \( \mu \) is the mobility.\(^{33}\) The pure Sb\(_2\)Te\(_3\) films, synthesized by the sputtering in this study and also by the coevaporation\(^{10,22,29}\) and MOCVD\(^{25}\) in the literature, generally exhibited higher \( \alpha \) but lower \( \sigma \) than those of bulk crystals.\(^{11,34-38}\) This could be due to the enhanced scattering of charge carriers at interfaces with decreasing thickness.\(^{10}\) Although the general inverse relationship between \( \alpha \) and \( \ln \sigma \) was observed for the pure Sb\(_2\)Te\(_3\) data (thin films and bulk crystals), a linear regression plot with the theoretical slope of \( k_B/e \sim 86.14 \mu V K^{-1} \) could not be obtained. The variation in the slope for different materials at different conditions was also observed previously,\(^{32}\) and more analysis about the \( \alpha - \ln \sigma \) relation is provided in Fig. S9 (ESI\(^+\)). The \( \alpha \) of GRP-Sb\(_2\)Te\(_3\) 10 nm was greater than those of pure Sb\(_2\)Te\(_3\) thin films with equivalent conductivities demonstrating the decoupling and enhancement of both \( \alpha \) and \( \sigma \). Fig. 2d compares power factors obtained in this study with the control data in the literature. There was a large variation in the power factor of Sb\(_2\)Te\(_3\) specimens in the literature depending on the synthesis method. The power factor of Sb\(_2\)Te\(_3\) 10 nm fell within a similar range to those of high quality Sb\(_2\)Te\(_3\) specimens in the literature. The power factor of GRP-Sb\(_2\)Te\(_3\) 10 nm was 8.58 \( \times \) 10\(^{-5}\) W K\(^{-2}\) cm\(^{-1}\) which is 256% higher than that of Sb\(_2\)Te\(_3\) 10 nm and 111% higher than the best value of Sb\(_2\)Te\(_3\)-based thin films in the literature achieved by the MOCVD method.\(^{25}\) There are also previous publications where a similar approach with different materials employed to enhance power factors is described.\(^{38-41}\)

The thermoelectric figure of merit can be re-derived using eqn S4:\(^2\)

\[
zT = \frac{x^2/L}{1 + k_l/k_e} \quad (3)
\]

where \( L \) is the Lorenz factor for free electrons. It is clear that \( zT \) can be enhanced by reducing the \( k_l/k_e \) ratio. In extreme cases of very high \( k_e \) or very low \( k_l \), \( zT \) depends on \( k_e \) only.\(^2\) Although the precise measurement of \( k \) was not carried out in this study, the three general strategies for the reduction of \( k \), suggested by Snyder and Toberer,\(^2\) were experimentally implemented in our heterostructure bilayer. Firstly, the phonon scattering within each layer was significantly enhanced. The \( k \) of graphene is dominated by phonons since electronic contribution is negligible due to the relatively low carrier concentration, and it can be significantly decreased by defects, rough edges, and interaction with neighboring layers.\(^{14,16,42}\) The \( k \) of graphene on a SiO\(_2\) support was 600 W m\(^{-1}\) K\(^{-1}\) at room temperature which is lower than that of suspended graphene.\(^{15}\) In addition, when the graphene is sandwiched between the top material and SiO\(_2\), the \( k \) will be even lower. The significantly increased defects of monolayer graphene during the sputtering process are also expected to enhance the phonon scattering (Fig. 1e). The inherent disorder in interstitial sites as well as the preferential \( \alpha \)-axis orientation also decrease \( k_l \) of the binary telluride layer.\(^2,23\) Secondly, the bilayer has distinct substructures providing different functions. The high mobility graphene provides the electron-crystal electronic structure whereas Sb\(_2\)Te\(_3\) with a (00l) orientation forms the low-thermal conductivity region. Finally, phonons are scattered at the heterointerface.\(^2,30\) The acoustic mismatch between layers reduces \( k_l \).\(^{41}\) A significant thermal resistance at the interface of graphene was observed in a study of heat conduction across monolayer and few-layer graphenes.\(^{44}\) The high \( k \) of graphene in the literature is the in-plane thermal conductivity. A theoretical investigation of graphite using a Debye model demonstrates that the \( \alpha \)-axis thermal conductivity is 4 orders of magnitude smaller than that in the basal plane.\(^{45}\) This also supports a possible decrease in thermal transport at the interface of graphene.

The thermoelectric figure of merit of GRP-Sb\(_2\)Te\(_3\) 10 nm is shown as a function of \( k_l \) using eqn (3) (Fig. S10, ESI\(^+\)). The range of \( k_l \) was varied from 1.0 to 600 W m\(^{-1}\) K\(^{-1}\) in the
calculation. The $k$ of the compact bulk specimen of Sb$_2$Te$_3$ was used as a lower limit. The $k$ of graphene on a SiO$_2$ support (600 W m$^{-1}$ K$^{-1}$) was used as an upper limit. The $zT$ increased rapidly as $k_l$ decreased, and the value was as high as 1.6 when $k_l = 1.0$ W m$^{-1}$ K$^{-1}$. This does not mean that $k_l = 1.0$ W m$^{-1}$ K$^{-1}$ can be achieved by the bilayer film. However, the possibility of reducing $k_l$ by the above-discussed strategies is favorable to enhance $zT$. The precise $k$ needs to be experimentally measured in the future. It will be also interesting to carry out an experiment in the future by forming four high conductivity contact pads which cover both graphene and Sb$_2$Te$_3$ layers on the sample. This may confirm that the graphene layer can work as a high mobility tunnel for carriers.

In summary, the enhancement of both $z$ and $\sigma$ was achieved by constructing the $c$-axis preferentially oriented nanoscale Sb$_2$Te$_3$ film on monolayer graphene. The graphene substrate enabled the preferential crystal growth of the Sb$_2$Te$_3$ film by a simple sputtering method enhancing $z$. The external graphene layer also provided a highway for carriers due to the extremely high mobility. The $\sigma$ of the bilayer also increased resulting in a high power factor ($8.58 \times 10^{-5}$ W K$^{-2}$ cm$^{-1}$). However, the precise measurement of $k$ needs to be carried out in the future. The $zT$ may increase or decrease depending on $k$ in spite of the high power factor.

Acknowledgements

This research was supported by Basic Science Research Program (2011-0004463) and WCU (World Class University) program (R31-2008-0010229-0) through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology. One of us (Y.H.L.) acknowledges STAR-faculty program (2010-0029653) from NRF funded by MEST.

Notes and references