Designing Two-Dimensional Dirac Heterointerfaces of Few-Layer Graphene and Tetradymite-Type Sb$_2$Te$_3$ for Thermoelectric Applications

Woosun Jang,* Jiwoo Lee,† Chihun In,‡ Hyunyong Choi,§ and Aloysius Soon∥\textsuperscript{†,\#}

\textsuperscript{1}Department of Materials Science & Engineering and \textsuperscript{2}School of Electrical & Electronic Engineering, Yonsei University, Seoul 03722, Korea

Supporting Information

ABSTRACT: Despite the ubiquitous nature of the Peltier effect in low-dimensional thermoelectric devices, the influence of finite temperature on the electronic structure and transport in the Dirac heterointerfaces of the few-layer graphene and layered tetradymite, Sb$_2$Te$_3$ (which coincidently have excellent thermoelectric properties) are not well understood. In this work, using the first-principles density-functional theory calculations, we investigate the detailed atomic and electronic structure of these Dirac heterointerfaces of graphene and Sb$_2$Te$_3$ and further re-examine the effect of finite temperature on the electronic band structures using a phenomenological temperature-broadening model based on Fermi–Dirac statistics. We then proceed to understand the underlying charge redistribution process in this Dirac heterointerfaces and through solving the Boltzmann transport equation, we present the theoretical evidence of electron–hole asymmetry in its electrical conductivity as a consequence of this charge redistribution mechanism. We finally propose that the hexagonal-stacked Dirac heterointerfaces are useful as efficient p–n junction building blocks in the next-generation thermoelectric devices where the electron–hole asymmetry promotes the thermoelectric transport by “hot” excited charge carriers.

KEYWORDS: thermoelectrics, graphene, topological materials, heterointerfaces, density functional theory, finite-temperature statistics, Fermi–Dirac distribution

1. INTRODUCTION

After the successful exfoliation of graphene, many researchers have attempted to exploit the exotic electronic structure of this two-dimensional (2D) nanomaterial by tuning and modulating the energy levels of its linear Dirac cone. The same can be said for another class of Dirac materials, the topological insulators (TIs), in which their time-reversal symmetry-protected topological surface states exhibit a linear Dirac cone energy–momentum dispersion, and they are also extensively investigated for their equally fascinating quantum properties.

Graphene was first suggested as an almost ideal material for thermoelectric applications, given its high flexibility, carrier mobility, and theoretical ZT value.\textsuperscript{5,9} Unfortunately, pristine graphene alone could not be used independently in thermoelectric devices due to high thermal conductivity.\textsuperscript{10} Recent studies have also demonstrated and discussed that the stacking sequence and thickness of multilayered graphene can strongly affect its electronic structure in different unexpected ways. For instance, AA-stacked graphene shows two separated Dirac cones with an enlarged energy band gap, whereas the AB-stacked (or the so-called Bernal-stacked) graphene displays parabolic bands rather than preserving its sharp linear Dirac cones.\textsuperscript{11} Similarly, for the trilayer graphene system, the hexagonal- (AAA-), Bernal- (ABA-), and rhombohedral- (ABC-) stacked graphene systems show very distinct electronic band dispersions as compared to its single-layer counterpart.\textsuperscript{12,13}

It was only recently reported that the so-called van der Waals epitaxial heterointerface structures (composed of graphene and metal chalcogenides) exhibit a dramatic improvement over the pristine components, owing to its very high thermoelectric power factor.\textsuperscript{14,15} These van der Waals epitaxial heterointerface systems may indeed be a game changer in the field of thermoelectrics. Motivated by experimental advances in the synthesis methods for the 2D Dirac multilayered graphene-based heterojunctions, the graphene/TI heterostructures are intensively studied.\textsuperscript{16–18} Owing to a small lattice mismatch (≈1–3\%) and the presence of heavy atomic species, TIs such as Sb$_2$Te$_3$ and Bi$_2$Te$_3$ are widely chosen as the contact substrate for graphene. Much attention has also been given to the carrier transport behavior in these 2D heterostructures where the enhanced spin–orbit coupling (SOC) and proximity effects are reported to be beneficial.\textsuperscript{19,20}

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 Specifically, in epitaxially grown graphene–Sb$_2$Te$_3$ heterointerfaces, the presence of graphene aids the growth of Sb$_2$Te$_3$ with superior crystallinity (where previously known structural defects are greatly minimized). This high crystallinity of epitaxially grown Sb$_2$Te$_3$ films results in a low defect concentration (and thus, low carrier concentration), which then explains the high Seebeck coefficient observed. Specifically, the heterointerface of graphene–Sb$_2$Te$_3$ boasts a 38 and 413% increase in its Seebeck coefficient (when compared to pristine Sb$_2$Te$_3$ and graphene, respectively), whereas its thermoelectric power coefficient has a colossal increase of 256 and 111% when compared to pristine Sb$_2$Te$_3$ and other Sb$_2$Te$_3$-based thin films.

However, the direct measurements of the thermoelectrical properties in these graphene/TI-based systems are often technically challenging due to the natural occurrence of the Peltier effect, which is caused by the temperature gradient between two current probes when an electrical current passes through the sample. Specifically, this temperature gradient set up via the Peltier effect in turn generates a Peltier voltage that results in a less accurate determination of the measured voltage. The Peltier voltage for a small amount of current is normally of the same order of magnitude as the resistive voltage. Moreover, other technical uncertainties, e.g., the exact positions of the probes and modes of contact, may further hinder a precise measurement of the electrical conductivity of these thermoelectric materials.

Given the ubiquitous nature of the Peltier effect, it is somewhat unsettling to know that a complete microscopic (i.e., atomic scale) understanding and description of these electrons with a finite temperature in low-dimensional thermoelectric nanomaterials is still very much lacking. However, it becomes immediately apparent that a rigorous theoretical treatment of these heavy-metal-containing heterointerfaces (e.g., SOC−inclusion electron−phonon coupling calculations from first principles) can easily become computationally prohibitive.

Thus, as a first step in this work, we will perform the first-principles density functional theory (DFT) calculations in conjunction with a phenomenological model to re-examine the finite-temperature electronic band structures of few-layer graphene/Sb$_2$Te$_3$ heterointerfaces.

2. METHODS

All of the density functional theory (DFT) calculations are performed using periodic boundary conditions, with the projector-augmented wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP). The generalized gradient approximation due to Perdew−Burke−Ernzerhof (PBE) is used to treat the exchange-correlation energy, augmented with the Grimme’s D2 van der Waals correction (PBE + D2) scheme. For the Brillouin zone integrations, a Γ-centered k-point grid of 12 × 12 × 1 is used for all of the calculations, with the exception of a much denser grid of 24 × 24 × 1 employed for solving the semiclassical Boltzmann transport equation (BTE) within the constant relaxation time approximation, as implemented in the BoltzTraP program. All of the DFT calculations are carefully tested for convergence with respect to the kinetic energy cutoff, k-point grid, vacuum region between repeated slabs, and substrate quintuple layer (QL) thickness, where the total energies and forces do not vary for more than 20 meV Å$^{-1}$. A planewave kinetic energy cutoff of 400 eV and a vacuum separation of at least 20 Å in the z direction are employed for the slab calculations. Spin−orbit coupling (SOC) is considered only for the electronic structure analysis. We relax the atomic coordinates for all of the structures and because asymmetric slabs are used in this work, a dipole correction (along the z direction) is employed for all of the slab calculations.

3. RESULTS AND DISCUSSION

3.1. Atomic Structures and Interfacial Energetics. To investigate the few-layer graphene/TI heterointerface structure, antimony telluride, Sb$_2$Te$_3$ (where its PBE + D2 optimized $a_0 = 4.24$ Å), one of the layered tetradymite (V$_x$Te$_y$), is selected as a representative TI substrate for graphene. To minimize the effect of lateral strain of graphene on Sb$_2$Te$_3$, a $\sqrt{3} \times \sqrt{3}$ R30$^\circ$ surface supercell of few-layer (i.e., monolayer, bilayer, and trilayer) graphene is stacked on Sb$_2$Te$_3$ (see Figure 1a). Here, the surface lattice constant, $a_0$ of stacked graphene is 4.27 Å, yielding only a small lattice mismatch of 0.7% for the graphene/TI heterointerfaces considered in this work. Thus, we choose to fix the interface lattice parameter of the graphene/TI to that of the TI.

For the single-layer graphene (so-called the “A” form), it has been determined to be the most energetically favored (and experimentally observed) interface structure where the outermost Te surface atom of Sb$_2$Te$_3$ is located at the center of the hexagonal ring of carbon atoms in graphene (so-called P1 site). Both the Bernal (AB) and hexagonal (AA) in the bilayer graphene are then considered by building on top of the single-layer graphene. This is followed by examining the hexagonal (AAA), Bernal (ABA), and rhombohedral (ABC) forms of the trilayer graphene stacked on the substrate (as shown in Figure 1b). To aid our discussion, we intuitively label our graphene/TI heterointerfaces as, e.g., grABC/Sb$_2$Te$_3$ for the rhombohedral trilayer graphene on Sb$_2$Te$_3$.

The interlayer spacings between the adjacent graphene layers and between the bottommost graphene and the uppermost surface Te atom of Sb$_2$Te$_3$ are measured and reported as $d_1$ and $d_2$, respectively (see Figure 1c). We find that although $d_2$ remains almost constant (i.e., 3.46 Å) for all of the few-layer graphene/Sb$_2$Te$_3$ heterointerfaces considered here, a larger $d_1$
value of 3.50 Å is found for the hexagonal bilayer (AA) and trilayer (AAA) graphene on Sb\textsubscript{2}Te\textsubscript{3} compared to the smaller measured value of 3.25 Å for the others. Our calculated structural parameters for the stacked graphene layers agree well with previous reports\textsuperscript{19,44,45}.

To determine the relative adsorption/adhesion strength of the few-layer graphene on Sb\textsubscript{2}Te\textsubscript{3} as a function of thickness and stacking sequence of the graphene, we calculate the work of adhesion, $W_{ad}$, normalized by the interface area, $A$, according to

$$W_{ad} = \frac{1}{A} \left( E_{SbTe_{3}}^{slab} + E_{gr}^{i} - E_{gr/SbTe_{3}}^{inf} \right)$$  \hspace{1cm} (1)

where $E_{SbTe_{3}}^{slab}$, $E_{gr}^{i}$, and $E_{gr/SbTe_{3}}^{inf}$ are the total DFT energies of the pristine 4 QL Sb\textsubscript{2}Te\textsubscript{3} slab, the free-standing few-layers graphene (with $i$ denoting the different A, AA, AB, AAA, ABA, and ABC stacking sequence), and the combined few-layer graphene/Sb\textsubscript{2}Te\textsubscript{3} heterointerfaces, respectively.

As shown in Table S1 in the Supporting Information, the value of $W_{ad}$ is found to be higher for the few-layer graphene on Sb\textsubscript{2}Te\textsubscript{3} as compared to that for the single-layered case. In particular, the $W_{ad}$ of the bilayer graphene/Sb\textsubscript{2}Te\textsubscript{3} systems are slightly higher than that of the trilayered ones (especially within the same stacking order). This may be rationalized by the weak repulsive interaction between the second and third graphene layers where net negative charges build up (see Figure 3c), and thus lowering the $W_{ad}$ of the trilayered systems. Taking the relative $W_{ad}$ for among the bilayer (and trilayer) graphene/Sb\textsubscript{2}Te\textsubscript{3} heterointerfaces, and the well-known weak van der Waals bonding between the graphene layers, we find only marginal differences ($<$0.5 meV Å\textsuperscript{-2}) and may conclude that the stacking orders do not strongly affect the energetics of these heterointerfaces.

We would like to further suggest that with such small energy differences, thermal contributions (even at room temperature and above) may well easily change the specific graphene stacking sequence for the bilayer and trilayer systems. Thus, in this work, we proceed to survey the specific electronic structure and properties of these few-layer graphene/Sb\textsubscript{2}Te\textsubscript{3} heterointerfaces with the inclusion of SOC and thermal effects.

### 3.2. Electronic Band Structures of Few-Layer Graphene and Sb\textsubscript{2}Te\textsubscript{3}

Before considering the electronic structure of these few-layer graphene/Sb\textsubscript{2}Te\textsubscript{3} heterointerfaces, we will discuss briefly the electronic structure of the TI substrate, Sb\textsubscript{2}Te\textsubscript{3}, as well as free-standing few-layer graphene.

From our previous work\textsuperscript{46} and other reports\textsuperscript{19,46}, the band structure (and topology) of the layered tetradymite (V\textsubscript{2}VI\textsubscript{3}) family is known to show a strong correlation not only on its stacking sequence but also on its number of QL where the zero-gap topologically nontrivial surface states will only emerge when this number exceeds a certain critical value. The fundamental band gap of Sb\textsubscript{2}Te\textsubscript{3} is reported to be around 0.14–0.28 eV\textsuperscript{46}. With the inclusion of SOC effects, Sb\textsubscript{2}Te\textsubscript{3} shows a drastic decrease in the band gap energy as its number of QL increases, and forms a nontrivial topological surface state at Γ-point when the thickness of the film becomes more than its topological critical thickness. Specifically, this minimum critical QL number for Sb\textsubscript{2}Te\textsubscript{3} is reported to be around 4–5.\textsuperscript{19,46,47} Hence, we have opted to use a minimum 4 QL Sb\textsubscript{2}Te\textsubscript{3} model in this work as the substrate for stacked graphene to investigate the influence of Sb\textsubscript{2}Te\textsubscript{3}'s nontrivial band topology on graphene. The electronic band structure (with SOC) of 4 QL Sb\textsubscript{2}Te\textsubscript{3} is plotted in Figure S1 of the Supporting Information.

Likewise, the electronic structure of free-standing few-layer graphene is known to show a strong dependency on both the number of atomic layers as well as its stacking sequence\textsuperscript{12,13}. Other structural modifications, e.g., morphological defects and mechanical strains have also been noted to exert an influence on its electronic properties\textsuperscript{12,13}. As clearly shown in our calculated band structures of the free-standing few-layer graphene structures (in the Supporting Information, Figures S1 and S2), and in agreement with other reports\textsuperscript{12,13}, the hexagonal-stacked graphene, i.e., gr\textsubscript{AA}, gr\textsubscript{AAA}, and gr\textsubscript{AAA} display their Dirac cones (as a multiple of the number of stacked layers) near the Fermi level. A microgap opening is also found for gr\textsubscript{AA} (30 meV) and gr\textsubscript{AAA} (10 meV) within the PBE + D2 approximation. This is in contrast to that found for the Bernal and rhombohedral graphene where clear parabolic bands are found near the Fermi level, with the known exception for gr\textsubscript{ABAB} which possesses both parabolic and linear energy dispersions\textsuperscript{12,13}.

#### 3.3. Phenomenological Temperature-Broadening Model

Now, we turn our attention to the electronic structure of these few-layer graphene/Sb\textsubscript{2}Te\textsubscript{3} heterointerfaces, and how finite-temperature effects may potentially alter their interface band structures.

To consider thermoelectric transport in the graphene/Sb\textsubscript{2}Te\textsubscript{3} heterointerfaces, a rigorous theoretical approach to account for all electron–phonon interactions from first-principles\textsuperscript{28} is generally desired but computationally demanding. Instead, we approach this problem by phenomenologically modeling the temperature effect via a statistical treatment of temperature-broadened electron occupancies in our band structure calculations at specific temperatures\textsuperscript{49}.

According to the Fermi–Dirac statistics, an elevated temperature results in a broadened distribution of electrons. To include the effect of temperature in our band structure calculations, we employ a Fermi–Dirac smearing function (which mimics the grand-canonical extension to DFT due to Mermin\textsuperscript{50} to approximate this broadening effect\textsuperscript{51,52} and use a Gaussian normal distribution to represent weight in the momentum–energy space. We then use a convolution between the two distribution functions to obtain a temperature-broadened projected electronic band structure.

Specifically, once the DFT eigenvalues in the ground-state projected band structures are determined, we apply this temperature broadening in two steps. We first project the band occupancies via a normal distribution, $\Gamma$, along the energy axis, $E$, using

$$\Gamma = \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{E^2}{2\sigma^2}\right)$$  \hspace{1cm} (2)

where our broadening parameter, $\sigma$, is defined as the product of the Boltzmann constant and the absolute temperature (i.e., $k_B T$).

In a similar fashion to the previous work using the Gaussian smearing function,\textsuperscript{49} we adopt the smearing function based on the Fermi–Dirac distribution\textsuperscript{50} with the following equation

$$f\left(\frac{E - \epsilon}{k_B T}\right) = \frac{1}{\exp\left(\frac{E - \epsilon}{k_B T}\right) + 1}$$  \hspace{1cm} (3)
where \( \epsilon \) denotes the eigenvalues. Then, we perform the final weighted-projection upon the energy axis for each \( k \)-point with

\[
\xi(E, T) = \omega f \otimes \Gamma \tag{4}
\]

Here, the temperature-dependent broadening of the band occupancy is reflected by the convolution of the Fermi–Dirac smearing and normal distribution functions (i.e., \( f \) and \( \Gamma \), respectively) multiplied by the calculated weight, \( \omega \). In our finite-temperature approach, the broadening parameter \( k_B T \) is about 0.05 eV at 600 K, in accordance with the variance range of the explicit phonon-induced band structure calculations.

As shown in Figure 2, the 0 K electronic band structures for \( gr_{A}/Sb_{2}Te_{3} \), \( gr_{AA}/Sb_{2}Te_{3} \), \( gr_{AB}/Sb_{2}Te_{3} \), \( gr_{AAA}/Sb_{2}Te_{3} \), and \( gr_{ABC}/Sb_{2}Te_{3} \) are plotted in the top panel, whereas that at 300 and 600 K are displayed in the middle and bottom panels of Figure 2, respectively.

At the outset, we first examine the electronic band structures of these heterointerfaces without the temperature effects (as in the upper panel of Figure 2). To discuss and compare the changes in the electronic band structure of these heterointerfaces with respect to the free-standing graphene and \( Sb_{2}Te_{3} \), we project the computed wavefunctions at each \( k \)-point of the band structure onto a set of orthogonalized pseudoatomic orbitals (as determined within the PAW potential used). This allows us to trace (and color-code) the contributions coming from either the graphene layer(s) or the \( Sb_{2}Te_{3} \) substrate (see Figure S3 of the Supporting Information).

Depending on the coupling strength of electronic states between the graphene layer(s) and \( Sb_{2}Te_{3} \), the computed wavefunctions may be strongly delocalized (system-dependent), and thus assigning such contributions unambiguously can be challenging and may not always be apparent. To complicate matters, the inclusion of SOC effects splits the bands further and hinders a straightforward comparison. Thus, to assist our discussions below, we have chosen to focus on a schematic description of the electronic band structure of these heterointerfaces (in the lower panel of Figure S3 in the Supporting Information).

We find that the overall band dispersions for the few-layer graphene is generally maintained when compared to their free-standing counterparts. They experience a small band gap opening and the splitting of degenerate states near the Fermi level (\( \epsilon_f \)) due to the proximity effect as discussed by others, \(^{19,20,53} \) as well as, especially for the hexagonal-stacked graphene layer(s), a displacement of the Dirac cones to a lower energy (i.e., \( n \)-doped).

Upon injecting the electrons from \( Sb_{2}Te_{3} \) to the graphene layers, the topological surface states of \( Sb_{2}Te_{3} \) begin to interact with Dirac cones of graphene, displaying several signatures of SOC effects in graphene’s band structure. Beside the opening of the band gap energy, we find the fourfold degenerate states

![Figure 2. Temperature-broadened electronic band structure of various few-layer graphene/Sb\(_2\)Te\(_3\) heterointerfaces: (left to right) gr\(_A\)/Sb\(_2\)Te\(_3\), gr\(_AA\)/Sb\(_2\)Te\(_3\), gr\(_AB\)/Sb\(_2\)Te\(_3\), gr\(_AAA\)/Sb\(_2\)Te\(_3\), gr\(_ABA\)/Sb\(_2\)Te\(_3\), and gr\(_ABC\)/Sb\(_2\)Te\(_3\), with a finite temperature of 0 K (upper panel), 300 K (middle panel), and 600 K (bottom panel) presented (with the SOC effect included). The vertical energy scale is set to 0 at the Fermi level, \( \epsilon_f \). The effect of finite temperature is approximated and applied using a convolution between a Fermi–Dirac smearing function and a normal distribution function (cf. eqs 2–4).](image-url)
(and their multiple) in gr/Te/Sb, and other bilayer and trilayer graphene in this work) begin to split under the influence of the SOC effect, producing Rashba-type split states\textsuperscript{54-56} in both the valence and conduction bands. These observations are very much in-line with other DFT + SOC calculations\textsuperscript{18,19} and tight-binding models\textsuperscript{20} where the TI substrate invokes these SOC-induced changes in the overall band structure of graphene layer(s). With regard to the energy bands of Sb, we find a general upshifting of the bands near ε\textsubscript{f} (i.e., p-doped) and also the classic signature of Rashba SOC interactions, e.g., in the cases of gr/Te/Sb and gr/Te/Sb, where Dirac and Kramers points are clearly illustrated near ε\textsubscript{f}.

Returning to Figure 2, we will now turn to the effect of finite temperature on the electronic band structures of these heterointerfaces. As outlined above, we do this phenomenologically via a statistical treatment of temperature-broadened DFT eigenvalues in our band structure calculations at both 300 and 600 K. Here, we find that with the inclusion of finite-temperature effects, the DFT eigenvalues are broadened and smoothed out, causing many of the SOC effects mentioned above to be no longer that apparent. However, we do observe that these temperature-broadened band structures (especially obvious for the ones modeled at room temperature of 300 K in the middle panel) retain the overall dispersion and characteristics of the 0 K ones. This is especially evident for the Dirac cones of the graphene layer(s), where the linear dispersions are hardly affected (albeit slightly down-shifted to lower energies).

Overall, from Figure 2, for all of the temperatures, we find that the overall band structures of these few-layer graphene/Te/Sb heterointerfaces strongly suggest a charge redistribution across the vdW layer between graphene layer(s) and SbTe, resulting in a p-doped SbTe and n-doped graphene heterojunction, particularly for the hexagonal-stacked systems. For a better understanding of this charge redistribution, we next proceed to calculate and examine the difference in the electron density between the graphene layer(s) and SbTe and further correlate how this charge redistribution might assist in the thermoelectric properties of these heterointerfaces.

### 3.4. Interfacial Charge Redistribution between Few-Layer Graphene and SbTe3

To examine the nature of bonding and charge redistribution between the few-layer graphene and SbTe, we calculate the difference in electron density (Δρ), where

\begin{equation}
\Delta \rho = \rho_{\text{gr}/\text{Te}/Sb} - \rho_{\text{gr}} - \rho_{\text{Te}/Sb}.
\end{equation}

Here, \( \rho_{\text{gr}/\text{Te}/Sb} \) is the total electron density of the combined few-layer graphene/Te/Sb heterointerfaces from which the electron density of both clean SbTe and substrate slab, \( \rho_{\text{Te}/Sb} \), and free-standing few-layers graphene, \( \rho_{\text{gr}} \), are subtracted while keeping their respective atomic positions to be the ones of the corresponding geometry-relaxed system. Furthermore, to obtain the planar-averaged difference electron densities (Δ\( \rho \)), electron densities are projected in one dimension along the out-of-plane direction (i.e., z direction) to rationalize the charge redistribution between the few-layer graphene and SbTe. Subsequently, we also perform an integration of \( \int \rho_{\text{avg}}(z) \) (i.e., \( \int \Delta \rho_{\text{avg}}(z) \)) to further analyze this charge redistribution at the heterointerface. We will focus on the hexagonal-stacked gr/Te/Sb, gr/Te/Sb, and gr/Te/Sb, to discuss on the trends in charge redistribution involving the Dirac cones of graphene.

The calculated Δ\( \rho \) and \( \int \rho_{\text{avg}}(z) \) (and its integrated form) for the hexagonal-stacked graphene layer(s) are presented in Figure 3. The most evident feature of charge redistribution in these heterointerfaces is the strong asymmetric accumulation/depletion of electrons near the van der Waals gap, i.e., the vertical void between the graphene layer(s) and SbTe. This is also clearly shown by the highest peak in the \( \int \Delta \rho_{\text{avg}}(z) \) for each heterointerface in Figure 3d.

In the case of the graphene layer that is closest to SbTe, the charges are very asymmetrically polarized (i.e., the small gain in electrons by the C atoms (red) sandwiched between the losses in electrons (blue) on both surfaces of this graphene layer). It is easy to deduce that this asymmetric polarization of charges for the closest graphene layer is due to the proximity effect of this graphene layer to the surface of SbTe, where an internal electrostatic field is generated by the potential gradient near the graphene/SbTe interface. This polarizing field is also known to account for the giant SOC interaction induced in the graphene in contact. In passing, this is in contrast to the case where graphene is sandwiched between two TI layers where symmetric polarization is reported.\textsuperscript{58}

Turning to their differences, by looking at the region just after the vdW gap (highlighted in pale green) in Figure 3d, the \( \int \Delta \rho_{\text{avg}}(z) \) differs for all of the three hexagonal-stacked...
heterointerfaces, suggesting that the electronic conductivity and thermoelectric transport for the few-layer graphene on Sb$_2$Te$_3$ may indeed be quite unlike that of the monolayer. To provide a perspective of how the thermoelectric properties of these few-layer graphene may change in the presence of Sb$_2$Te$_3$, we solve the Boltzmann transport equation (BTE) (via the BoltzTraP program$^{36}$) and present our results for both the pristine free-standing hexagonal-stacked graphene and gr$_{AA}$/Sb$_2$Te$_3$, gr$_{AA}$/Sb$_2$Te$_3$, and gr$_{AAA}$/Sb$_2$Te$_3$, respectively, in Figure 4a,b.

Figure 4. Calculated electrical conductivity ($\sigma/\tau$, measured in 1/Ω m s) of (a) free-standing pristine graphene layer(s) and (b) few-layer graphene/Sb$_2$Te$_3$ heterointerface structures within the relaxation time approximation. Both free-standing and interface structures with gr$_{AA}$, gr$_{AA}$, and gr$_{AAA}$ are depicted in black, orange, and red lines, respectively. (c) Schematic diagram to illustrate a possible thermoelectric device structure, consisting of Sb$_2$Te$_3$/graphene p–n heterointerface structure. Blue, red, and gray boxes denote graphene, Sb$_2$Te$_3$, and heat absorber/rejector components, accordingly.

3.5. Electron–Hole Asymmetry in Electrical Conductivity Simulations. We first begin by Briefly outlining how we calculate the electrical conductivity of both free-standing and supported graphene layer(s). By solving the semiclassical Boltzmann transport theory within the constant relaxation time approximation, the group velocities of the charge carriers are first obtained from the electronic band structure via the relation $v(i, k) = \frac{e}{\hbar} \nabla_{k} E(i, k)$, where $i$, $k$, and $\hbar$ denote the band index, wave vector, and reduced Planck constant, respectively. Within the relaxation time approximation, the transport distribution function tensor is then calculated with the equation $\bar{\sigma}_{ij}(\epsilon) = \frac{1}{N} \sum_{i,k} n_{i}(i, k) u_{i}(i, k) \frac{\partial \rho_{c}(\epsilon, i, k)}{\partial \epsilon}$, where $\alpha$ and $\beta$ are the tensor indices. Based on the transport distribution tensor, the electrical conductivity tensor can be calculated from the equation $\sigma_{ij}(T, \mu) = \frac{1}{\Omega} \int \bar{\sigma}_{ij}(\epsilon) \left[ -\frac{\partial \rho_{c}(T, \epsilon, \mu)}{\partial \epsilon} \right] \mathrm{d}\epsilon$, where $\Omega$, $\mu$, and $f_{0}$ denote the unit cell volume, the electron chemical potential of carriers, and the Fermi–Dirac distribution function of the carriers, respectively.

Here, we can find some interesting physical insights from solving the BTE. In Figure 4a, we calculated the electrical conductivity for the pristine free-standing graphene layer(s) is close to perfectly symmetric about the zero value of the electron chemical potential, $\mu$, i.e., having no electron–hole asymmetry. As we go from a monolayer to the bilayer and then to the trilayer for the hexagonal-stacked graphene, we see a rather dramatic symmetrical increase in the $\sigma$ value by $2-3$ orders of magnitude (i.e., between $10^{18}$ and $10^{20}$ (Ω m s)$^{-1}$, noting that it is plotted in the log scale). This tells us that the (thermo)electric transport behavior of pristine few-layer graphene should be very similar in both the electron and hole regimes, whereas we will then see that this is very much a different picture for the few-layer graphene/Sb$_2$Te$_3$ heterointerfaces.

Referring to Figure 4b, here we plot the same electrical conductivity for the few-layer graphene/Sb$_2$Te$_3$ heterointerfaces, but on a slightly different scale range. We first notice that the electrical conductivity behavior of heterointerfaces is very asymmetric about the zero value of $\mu$, and these conductivities are way much higher than their free-standing counterparts ($\sim 10^{20}$ (Ω m s)$^{-1}$ and above). In pristine few-layer graphene structures, it is clear from their band structures that the conduction and valence bands are symmetric (as reflected in the Dirac cones in Figures S1 and S2). This corroborates the symmetric electrical conductivity plots (in Figure 4a), where $\mu$ relates to the Fermi level in our DFT band structure calculations. From our finite-temperature DFT band structure calculations, we find that the hexagonal-stacked heterostructures are mildly n-doped, hence left-shifting the electrical conductivity plots (in Figure 4b). This also results in the observed asymmetry (in part, due to the charge redistribution).

Returning back to our earlier discussion of thermoelectric relations in low-dimensional nanomaterials, recent studies on the interfacial charge transfer to graphene from electrode contacts$^{62,63}$ have further supported that electron–hole asymmetry (as deduced from experimentally determined current/voltage (I/V) curves) is beneficial for setting up an efficient thermoelectric p–n junction.

Particularly, for the AA-graphene/Sb$_2$Te$_3$ heterointerface, as shown in Figure 4b, its lower electrical conductivity may be accounted for by the difference in polarization of the graphene layers (as shown in Figures 3 and S5 of the Supporting Information). Here, we find the polarization results in a clear charge redistribution of the graphene layers, and we suggest that this could confine the carriers between the electrostatically attractive field setup by these charge layers (see Figure S5). Our calculated $\Delta \rho$ plots suggest that a larger concentration of charge carriers is confined between all vdW gaps in the AA-graphene/Sb$_2$Te$_3$ interface than in the A- and AA-stacked heterointerfaces. We attribute the presence of higher charge carriers confined in the vdW gaps of AA-stacked heterointerface to the lower electrical conductivity of the AA-stacked heterointerface, as compared to the other two heterointerfaces.

Concluding, we would like to propose that the hexagonal-stacked few-layer graphene/Sb$_2$Te$_3$ heterointerfaces can be used as the p–n junction building blocks to construct an efficient thermoelectric device (as conceptually illustrated in Figure 4c) that exploits the electron–hole asymmetry by
enhancing the carrier transport with “hot” excited charge carriers.

4. SUMMARY

To summarize, using first-principles DFT calculations, we survey and investigate various graphene/Sb$_2$Te$_3$ heterointerfaces in different stacking sequences. Using the DFT(+D2) optimized atomic structures, we calculate the electronic band structures of these graphene/Sb$_2$Te$_3$ Dirac heterointerfaces, including the effects of SOC. We find that most essential topological band features are well reproduced; using a phenomenological temperature-broadening model based on the Fermi–Dirac statistics, we re-examine the effect of finite temperature on the electronic band structures. Consequently, we also find that the DFT eigenvalues are broadened and smoothed out with increasing temperature, obscuring many of the spin–orbit interactions. Nonetheless, it is evident that the Dirac cones of the graphene layer(s) are hardly affected (albeit slightly down-shifted to lower energies). From the calculated band structures, we identify the underlying charge redistribution process by analyzing the difference in electron densities to find large polarization effects at the interface, driving the charge redistribution of electrons between Sb$_2$Te$_3$ and graphene. When solving the Boltzmann transport equation for these heterointerfaces, we have also found a strong case for electron–hole asymmetry in its electrical conductivity as a signature of enhanced thermoelectric properties. In closing, we offer these graphene/Sb$_2$Te$_3$ Dirac heterointerfaces as useful p–n junction building blocks for the next-generation thermo-electric devices in which the carrier transport may be enhanced by “hot” excited charge carriers.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b09805.

Optimized structural parameters for each graphene/Sb$_2$Te$_3$ interface system; calculated electronic band structures of pristine Sb$_2$Te$_3$ and free-standing few-layer graphene systems; projected electronic band structure of various few-layer graphene/Sb$_2$Te$_3$ heterointerfaces (with and without the inclusion of spin–orbit coupling effect) (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: aloysisus.soon@yonsei.ac.kr.

ORCID
Woosun Jang: 0000-0003-1274-1714
Hyunyong Choi: 0000-0003-3295-1049
Aloysius Soon: 0000-0002-6273-9324

Notes
The authors declare no competing financial interest.

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Thermoelectric Properties of Individual Polycrystalline Bismuth Thin Films.


Supporting Information

Designing Two-Dimensional Dirac Heterointerfaces of Few-Layer Graphene and Tetradyminite-Type Sb$_2$Te$_3$ for Thermoelectric Applications

Woosun Jang,† Jiwoo Lee,† Chihun In,‡ Hyunyong Choi,‡ and Aloysius Soon*;†

†Department of Materials Science & Engineering, Yonsei University, Seoul 03722, Korea
‡School of Electrical & Electronic Engineering, Yonsei University, Seoul 03722, Korea

E-mail: aloysius.soon@yonsei.ac.kr
Table S1: Optimized structural parameters for each graphene/Sb$_2$Te$_3$ interface system: Interlayer spacings, $d_1$ and $d_2$ (in Å, cf. Figure 1c) are listed. $d_3$ is the interlayer distance between consecutive quintuple layers in Sb$_2$Te$_3$. The corresponding work of adhesion ($W_{ad}$, in meV Å$^{-2}$) and surface work function ($\Phi$, in eV) are also reported. Note that a positive value of $W_{ad}$ will indicate favorable adhesion/adsorption to the Sb$_2$Te$_3$ substrate. $\Phi$ of pristine Sb$_2$Te$_3$ and free-standing monolayer graphene are calculated to be 4.54 and 4.23 eV, respectively.

<table>
<thead>
<tr>
<th>Interface system</th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_3$</th>
<th>$W_{ad}$</th>
<th>$\Phi$</th>
</tr>
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<tbody>
<tr>
<td>gr$_A$/Sb$_2$Te$_3$</td>
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<td>3.46</td>
<td>2.93</td>
<td>14.448</td>
<td>4.24</td>
</tr>
<tr>
<td>gr$_{AA}$/Sb$_2$Te$_3$</td>
<td>3.50</td>
<td>3.46</td>
<td>2.93</td>
<td>15.484</td>
<td>4.01</td>
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<tr>
<td>gr$_{AB}$/Sb$_2$Te$_3$</td>
<td>3.25</td>
<td>3.46</td>
<td>2.93</td>
<td>15.910</td>
<td>4.30</td>
</tr>
<tr>
<td>gr$_{AAA}$/Sb$_2$Te$_3$</td>
<td>3.51</td>
<td>3.46</td>
<td>2.93</td>
<td>15.411</td>
<td>4.20</td>
</tr>
<tr>
<td>gr$_{ABA}$/Sb$_2$Te$_3$</td>
<td>3.24</td>
<td>3.45</td>
<td>2.93</td>
<td>15.634</td>
<td>4.24</td>
</tr>
<tr>
<td>gr$_{ABC}$/Sb$_2$Te$_3$</td>
<td>3.25</td>
<td>3.46</td>
<td>2.93</td>
<td>15.620</td>
<td>4.25</td>
</tr>
</tbody>
</table>

Figure S1: Calculated electronic band structures of pristine 4 QL Sb$_2$Te$_3$, free-standing gr$_A$, gr$_{AA}$, and gr$_{AB}$. The Fermi level is indicated by the dotted horizontal lines at 0 eV.
Figure S2: Calculated electronic band structures of free-standing gr_{AAA}, gr_{ABA}, and gr_{ABC}. The Fermi level is indicated by the dotted horizontal lines at 0 eV.

Figure S3: (Color online) Projected electronic band structure of various few-layer graphene/Sb$_2$Te$_3$ heterointerfaces: (left to right) gr$_A$/Sb$_2$Te$_3$, gr$_{AA}$/Sb$_2$Te$_3$, gr$_{AB}$/Sb$_2$Te$_3$, gr$_{AAA}$/Sb$_2$Te$_3$, gr$_{ABA}$/Sb$_2$Te$_3$, and gr$_{ABC}$/Sb$_2$Te$_3$, presented in the upper panel (with the SOC effect included). Bands due to the few-layer graphenes are colored in red. The corresponding decomposed band structure scheme (left: Sb$_2$Te$_3$; right: graphene) is plotted in the lower panel for each few-layer graphene/Sb$_2$Te$_3$ heterointerface. The Fermi level is indicated by the dotted horizontal lines at 0 eV.
Figure S4: (Color online) Projected electronic band structure of various few-layer graphene/Sb$_2$Te$_3$ heterointerfaces (without the SOC effect included): (left to right) gr$_A$/Sb$_2$Te$_3$, gr$_{AA}$/Sb$_2$Te$_3$, gr$_{AB}$/Sb$_2$Te$_3$, gr$_{AAA}$/Sb$_2$Te$_3$, gr$_{ABA}$/Sb$_2$Te$_3$, and gr$_{ABC}$/Sb$_2$Te$_3$. Bands due to the few-layer graphenes are colored in red. The Fermi level is indicated by the dotted horizontal lines at 0 eV.

Figure S5: (Color online) (a) Top view of the graphene/Sb$_2$Te$_3$ heterointerface. The C, Sb, and Te atoms are depicted as black, gray, and purple spheres, respectively. The pale black line and thick red line denotes the unit cell boundary and slicing plane for 2D projected difference electron density ($\Delta \rho$), accordingly. (b) Integrated planar-averaged $\int \Delta \rho_{\text{avg}}(z)$ as projected along the z-axis for gr$_A$/Sb$_2$Te$_3$, gr$_{AA}$/Sb$_2$Te$_3$, and gr$_{AAA}$/Sb$_2$Te$_3$, respectively (scaled up; cf. Figure 3d in the main text). 2D projected $\Delta \rho$ of (c) gr$_A$/Sb$_2$Te$_3$, (d) gr$_{AA}$/Sb$_2$Te$_3$, and (e) gr$_{AAA}$/Sb$_2$Te$_3$, respectively.