Control of Thermal and Electronic Transport in Defect-Engineered Graphene Nanoribbons

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Low-dimensional carbon-based nanomaterials, graphene1–4 and graphene nanoribbons (GNRs), have attracted extensive attention in recent years due to their extraordinary electrical,5–7 optical,8,9 thermal,10–14 and mechanical15,16 properties. The experimental room temperature (RT) carrier mobility (15,000–27,000 cm2 V–1 s–1), quantized electrical conductance, high Seebeck coefficient,17 extremely high RT thermal conductivity (κ) of graphene, and the ability to tune these properties by changing width and edge structure18–21 have motivated many scientists to consider graphene-based materials for future nanoscale device applications,22–25 including thermal management in nanoelectronics26,27 and thermoelectric power generation.28–32 Recent developments in fabrication techniques have made it possible to grow very narrow23,33 and atomically precise35 GNRs, further stimulating interest in this direction.

The room temperature thermal conductivity of graphene has been measured by several groups, and reported values range between 400 and 600 W/mK10,13 and 2500–5300 W/mK11–13 for the supported and suspended samples, respectively. The strong dependence of these values on the length and width of the samples can be attributed to the long RT phonon mean free path (MFP), which is reported to be around 750 nm.26 In addition to these experimental studies, a substantial theoretical effort based on several different techniques has been devoted to understand the thermal transport properties of both graphene36–39 and GNRs.40–49 The calculations confirm the experimentally predicted high values for κ at RT, particularly for the suspended graphene, and support the observed effects of width and length on thermal transport. Additionally, significant variations in κ of GNRs with edge termination have been predicted, where zigzag GNRs (ZGNRs) are found to be thermally more conductive than the armchair GNRs (AGNRs) having the same width and length.40,43,45,50,58 In spite of this serious theoretical effort, the effects of intrinsic defects, single and double vacancies, topological defects, edge termination, and level of roughness on κ of experimentally feasible GNRs have not been systematically studied as of yet. In particular, the extensive investigation of how these imperfections can be used to tune the resulting thermal transport would be enormously beneficial for future technological applications of GNRs.

On the other hand, the influence of these imperfections on the electronic transport is not parallel to the thermal case. The electronic...
Transport can exhibit surprising variations that depend on the type of defects, chirality, and edge structure. While edge roughness produces a decrease in the thermal transport through GNRs regardless of the chirality or width, its effect on electronic transport is more complex. The electronic transport through edge-roughened ZGNRs retains the quasi-ballistic transport characteristics of pristine GNRs; however, the quasi-ballistic nature of AGNRs is deteriorated significantly by the presence of only minute edge disorder. On the other end of the spectrum, bulk vacancies have been shown to reduce both the thermal and electronic transport at small concentrations, independent of the ribbon chirality. ZGNRs are of particular interest due to the fact that electrons in the first conduction plateau (FCP) are less sensitive to edge disorder, where phonons are strongly suppressed. This opposite behavior can give rise to a thermoelectric figure of merit (ZT) as high as 4 at room temperature. The principal aim of this study is to analyze the interplay between defects in GNRs and the resulting effects on thermal and electronic transport. We investigate each of these cases meticulously to obtain a better understanding of the transport properties and the possible independent control of them for potential applicability of GNRs as thermoelectrics. The findings then can be used as a guide for future experimental and theoretical work.

RESULTS AND DISCUSSION

Thermal Transport. The effect of randomly distributed single and double vacancies, Stone–Wales defects, and ribbon-edge terminations and level of roughness on the $\kappa$ of GNR structures having a width of $>15$ nm and a length of $>100$ nm are considered in this study. This requires simulations of systems (up to 300,000 atoms) that have experimental dimensions with rough edges and various structural defects, each of which affects thermal conductivity and the electronic properties differently. Figure 1 shows various structural aspects of GNRs that are investigated in this work, including rough edges, single vacancies, double vacancies, and Stone–Wales defects. To perform the lattice thermal conductivity calculations, we employ molecular dynamics and Green–Kubo formalism (see the Methods section). A reoptimized Tersoff parameter set ($) is used to represent graphene and GNRs. The original Tersoff parameter set $^2$ underestimates the frequencies of the acoustic phonon modes, while the RP produces a graphene phonon dispersion in good agreement with experiment. Of fundamental importance is that the RP captures the quadratic behavior of the lowest frequency phonon modes near the $\Gamma$ point. The OP produces linear behavior in this region, which may cause significant error in thermal conductivity. The significance of this difference is reflected by a 50–60% underestimation of the thermal conductivity of graphene by the OP when compared to the RP (Figure 2a). As a further note, the RT $\kappa$ produced by the RP, 2600 W/mK, is coherent with various experimental measurements and theoretical calculations. The slope of the lattice thermal conductivity shows a decreasing trend with temperature due to an increase in phonon population at higher energy states, resulting in an increase in phonon scattering.

Before discussing how edge and vacancy defects affect the $\kappa$ of GNRs, it is important to thoroughly understand the behavior of the pristine GNRs, including how the length of the simulated GNR influences the resulting thermal conductivity. Certain artificial size effects can arise in MD due to the periodic boundary conditions along the transport direction for the nanosystems. When the simulation size is too small for a nanosystem simulated using 1D or 2D periodicity, this periodicity leads to correlated scattering events which reduce the calculated thermal conductivity, requiring a systematic study of length dependence. A variety of studies have reached different conclusions on what dimension is sufficient for a GNR to be free from these spurious size effects, but most use a length on the order of tens of nanometers. The length dependence of $\kappa$ (see Figure 2b) suggests that the minimum length to attain a converged $\kappa$ value should be...
around 75–100 nm, as reflected in the results for ZGNRs with widths of 15 and 8 nm. At this limit, the RT \( \kappa \) for a 15 nm wide ZGNR is shown to reach 2300 W/mK. The ribbon width also produces a strong effect that can clearly be seen for both ZGNRs and AGNRs (Figure 2c). At a width of 4 nm, \( \kappa \) becomes quite small, 840 and 680 W/mK for ZGNRs and AGNRs, respectively, and the edge scattering becomes more pronounced. With increasing width values, the \( \kappa \) of both edge termination forms steadily rises, with the zigzag termination form always remaining higher, nearly twice that of the armchair value at 15 nm width. The low value of \( \kappa \) for the AGNRs is a result of its higher number of edge scatterers compared to the ZGNRs; that is, the armchair termination has more atoms per unit length than the zigzag termination, which effectively increases the influence of the edges on \( \kappa \). This persists until the width reaches 40 nm, after which the \( \kappa \) of both edge forms appears to converge to 2300 W/mK. This value is still 10% less than “infinite” graphene, suggesting that the approach to the graphene conductivity is gradual and requires much larger widths.

As evident from the difference in thermal conductivity of ZGNRs and AGNRs, the edge form/structure is a degree of freedom in modifying the thermal transport. Edge, in principle, is an extended defect and hence decreases the thermal conductivity. Roughness is another edge structure parameter that further modifies the average phonon mean free path by introducing additional scattering processes. In this study, the rough ribbon edges are randomly created with a target roughness value, and the coordination number is at least 2 for the edge carbon atoms. Naturally, for a higher roughness, there are more two-coordinated atoms for the ZGNRs. In Figure 1, a portion of one such ribbon edge with a roughness of 7.28 Å is shown. The thermal conductivity of the ribbon decreases with increasing roughness, as can be seen in Figure 3a. At room temperature, compared to smooth-edged ribbon of the same size, approximately an 80% reduction in the thermal conductivity value is observed for the highest roughness value. In addition, the data in Figure 3 show a drastic change in temperature dependence of \( \kappa \). As the roughness increases, the slope of the conductivity curve approaches zero, indicating dominance of the scattering due to roughness. An analogous observation can be made as the single vacancy concentration is increased to 0.05%
and above (see Figure 3b). The conductivity behaves much like defect-free ribbon for a vacancy concentration of 0.0001; however, the curve flattens when the vacancy concentration increases to 0.001. It is also noteworthy that, in extreme defect states, a very weak temperature-dependent behavior is observed with similar conductivity values.

For a more complete understanding of thermal transport in GNRs, the interplay between internal defect states and $\kappa$ should be further addressed. We focus on the three most common types of defects, shown in Figure 1: single vacancies, double vacancies, and Stone–Wales defects. A single vacancy, removal of one atom, is a high energy defect that leaves three carbon atoms two-coordinated, effectively breaking the sp² character of the local lattice. A double vacancy, removal of two atoms from the lattice, is more favorable than a single vacancy as the local structure rearranges to restore the three-coordinated sp² bonding to each atom by creating an octagon and two pentagon structure. Similarly, a Stone–Wales defect is a topological defect that preserves sp² bonding by forming a structure with two heptagons and two pentagons. Among the defect types we consider, the single vacancy has the most dramatic effect on $\kappa$ (Table 1). At very low concentrations, 0.0001 (corresponding to removal of 1 carbon atom out of 10 000), a 25% reduction in thermal conductivity is noted, while a concentration of 0.001 shows close to an 80% decrease from the values obtained for the pristine GNRs. However, a concentration of 0.001 for Stone–Wales and divacancies only reduces the thermal conductivity by 70%. To reach the 80% reduction, these concentrations must be increased to 0.0023. The underlying mechanism making single vacancies much more effective at reducing lattice thermal conductivity is intrinsically related to their less stable two-coordinated atoms. The two-coordinated atoms will be less likely to follow the normal pattern of vibrations in the pristine material and cause a higher degree of scattering. This point is further supported by the fact that the double vacancy and Stone–Wales defects have the same effect on thermal conductivity, and both have only sp² bonds. Even when Stone–Wales defects and double vacancies are mixed in a 1:1 ratio, the thermal conductivity remains the same as the pure double vacancy or Stone–Wales structure with the same concentration (Table 1). This weaker dependence of $\kappa$ on the Stone–Wales defects has also been noted for single-wall carbon nanotubes and SWCNT bundles.64

Table 1. Thermal Conductivity Results for Various Defected ZGNRs of 100 nm Length and 15 nm Width at Ambient Conditions (Percent Decrease from the Pristine Case Is Also Included)

<table>
<thead>
<tr>
<th>Type</th>
<th>Concentration</th>
<th>$\kappa$ (W/mK)</th>
<th>% Decrease</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td></td>
<td>2300</td>
<td></td>
</tr>
<tr>
<td>single vacancy</td>
<td>0.0001</td>
<td>1726</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>0.0005</td>
<td>943</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>0.0010</td>
<td>426</td>
<td>81</td>
</tr>
<tr>
<td>double vacancy</td>
<td>0.0010</td>
<td>707</td>
<td>69</td>
</tr>
<tr>
<td>Stone–Wales</td>
<td>0.0010</td>
<td>709</td>
<td>69</td>
</tr>
<tr>
<td>mix 50/50</td>
<td>0.0010</td>
<td>703</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>0.0017</td>
<td>612</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>0.0023</td>
<td>431</td>
<td>81</td>
</tr>
</tbody>
</table>

For a more complete understanding of thermal transport in GNRs, the interplay between internal defect states and $\kappa$ should be further addressed. We focus on the three most common types of defects, shown in Figure 1: single vacancies, double vacancies, and Stone–Wales defects. A single vacancy, removal of one atom, is a high energy defect that leaves three carbon atoms two-coordinated, effectively breaking the sp² character of the local lattice. A double vacancy, removal of two atoms from the lattice, is more favorable than a single vacancy as the local structure rearranges to restore the three-coordinated sp² bonding to each atom by creating an octagon and two pentagon structure. Similarly, a Stone–Wales defect is a topological defect that preserves sp² bonding by forming a structure with two heptagons and two pentagons. Among the defect types we consider, the single vacancy has the most dramatic effect on $\kappa$ (Table 1). At very low concentrations, 0.0001 (corresponding to removal of 1 carbon atom out of 10 000), a 25% reduction in thermal conductivity is noted, while a concentration of 0.001 shows close to an 80% decrease from the values obtained for the pristine GNRs. However, a concentration of 0.001 for Stone–Wales and divacancies only reduces the thermal conductivity by 70%. To reach the 80% reduction, these concentrations must be increased to 0.0023. The underlying mechanism making single vacancies much more effective at reducing lattice thermal conductivity is intrinsically related to their less stable two-coordinated atoms. The two-coordinated atoms will be less likely to follow the normal pattern of vibrations in the pristine material and cause a higher degree of scattering. This point is further supported by the fact that the double vacancy and Stone–Wales defects have the same effect on thermal conductivity, and both have only sp² bonds. Even when Stone–Wales defects and double vacancies are mixed in a 1:1 ratio, the thermal conductivity remains the same as the pure double vacancy or Stone–Wales structure with the same concentration (Table 1). This weaker dependence of $\kappa$ on the Stone–Wales defects has also been noted for single-wall carbon nanotubes and SWCNT bundles.64

Electronic Transport and Thermoelectric Properties. First, we investigate electronic transport through ZGNRs as a function of the spatial distribution of single vacancy defects. We perform the calculations for ZGNR(70), with 70 being the number of zigzag chains along the ribbon, which corresponds to a width of ∼15 nm. There are 140 atoms per unit cell, and 70 inequivalent vacancy positions ($v = 1, ..., 70$). The electronic transmission ($\tau$) in the presence of a single vacancy varies strongly depending on its position, $v$ (see Figure 4). If the vacancy is located within 7.5 Å of the edge of the ZGNR ($v < 7$), states within the FCP are also weakly affected, but edge-localized states at the charge neutrality point (CNP) are scattered strongly (Figure 4a). This is due to the fact that these edge states give rise to a singularity in the density of states (DOS) at the CNP65 and are therefore prone to defects located close to the edges. The opening of a transport gap at the CNP and quasi-ballistic behavior within the FCP were reported previously for ZGNRs with edge roughness,3,51 but to the best of our knowledge, similar behavior for vacancies close to the edges has not been reported before. As the single vacancy is positioned away from the edge ($v > 7$), states within the FCP are also scattered strongly (Figure 4b).

To better understand the electronic transport through defected GNRs, we investigate long ZGNRs with random distributions of single vacancies. Having obtained the transmission spectra of individual scatterers, we employ scattering theory which yields accurate results for dilute scatterers.66,67 in the diffusive
regime, the resistance due to each scatterer is additive; therefore, the transmission due to \( N \) vacancies is obtained according to

\[
\frac{1}{T_N} = \frac{1}{T_0} - \frac{N}{\sum_v N_v T_v},
\]

(1)

where \( R_o/2T_o \) is the contact resistance, \( T_o \) is the pristine transmission and \( R_o = h/e^2 \) is the quantum of resistance. \( T_v \) and \( N_v \) are the transmission amplitude and the number of vacancies with particular configuration \( v \), respectively, and \( N = \sum_v N_v \) is the total number of vacancies in a sample. In Figure 5a, transmission spectra are plotted for different numbers of single vacancies ranging between \( N = 10^1 \) and \( 10^4 \) as well as that of the pristine ribbon. Here, \( N = 10^3 \) corresponds to a ZGNR of length, \( L, 17.5 \mu \text{m} \) with a defect concentration of \( d = 0.001 \). We note that the transmission spectrum is symmetric around the CNP \((E = 0)\) due to electron hole symmetry of the Hamiltonian (see Methods). Single vacancies are most effective within the FCP, and sawtooth-like transmission profiles are observed for all \( N \). We also calculate the room temperature electronic conductance for \( N = 10^3 \) and \( N = 10^4 \) (Figure 5b). We note that the conductance is reduced by more than 2 orders of magnitude for \( N = 10^4 \), compared to the pristine ZGNR, but the conductance plateaus are still observable. Survival of conductance plateaus, even when conductance is suppressed dramatically, was measured previously.\(^{61}\) In a previous study, the emergence of the plateaus was assigned to be due to the enhanced backscattering by bulk vacancies.\(^{60}\) In that work, the calculations were carried out for AGNRs, and sawtooth-like transmission profile for bulk disorder was observed, similar to the profiles we observe for ZGNRs. Our calculations show that the survival of the conductance steps are independent of the edge shape being armchair or zigzag.

As an important step to better understand electronic transport in GNRs, we investigate how the degree of edge roughness affects both electronic transmission through the ribbon and the mean free path of the electrons. For a ZGNR with edge roughness, we employ a recursive Green's function scheme.\(^{68}\) We prefer the recursive scheme in order to include the multiple scattering effects due to the correlated and dense nature of edge roughness disorder. We calculate the transmission values of ZGNR(70) with edge roughness for various lengths of structures up to \( \sim 0.5 \mu \text{m} \) (2000 unit cells). In Figure 6a, we plot the electronic transmission values for sample lengths up to \( L = 125 \mu \text{m} \) with edge roughness \( R_{\text{rms}} = 1.98 \AA \). The transmission values for \( L > 0.5 \mu \text{m} \) are obtained by averaging over 25 representative structures of the desired edge roughness, as defined by the same algorithm in Figure 3. For \( L > 0.5 \mu \text{m} \), we use the elastic mean free paths \( l(E) \) to predict the transmission values. The mean free paths are obtained from the ensemble-averaged transmission spectra using

\[
T(E,L) = T_p(1 + L/l(E))^{-1},
\]
where \( \mathcal{T}_p \) is the transmission of the pristine ribbon. In Figure 6a, one observes that transmission drops rapidly with length, except for the energy values \( E < 0.17 \text{ eV} \), and the reduction is more rapid for higher energies. This suppression is clearly visible in the energy dependence of \( \mathcal{T} \) in Figure 6b. For \( R_{\text{rms}} = 1.98 \text{ Å} \), \( \mathcal{T} \) is always longer than 10 \( \mu \text{m} \) within the FCP (\( E < 0.17 \text{ eV} \)), reaching a value of 100 \( \mu \text{m} \), then dropping rapidly with increasing energy and making dips at the band edges. The \( \mathcal{T} \) is shorter for higher \( R_{\text{rms}} \) at all energies. It is still considerably larger in the FCP compared to the rest of the spectrum for \( R_{\text{rms}} = 4.44 \text{ Å} \), but this behavior is reversed when \( R_{\text{rms}} = 7.38 \text{ Å} \). We assign this behavior to the fact that transmission within the FCP is preserved only when vacancies are within 7.5 Å of the edge (\( v \leq 7 \)). In other words, when \( R_{\text{rms}} \) increases to 7.38 Å, the amplitude of the roughness can breach the 7.5 Å region at the edge, causing significant scattering in the FCP.

Comparing edge roughness with bulk vacancies, we note the destructive nature of bulk vacancies at low energies, while the quasi-ballistic transport through rough ZGNR with small \( R_{\text{rms}} \), together with depressed lattice thermal conductivity of these structures, implies good thermoelectric properties. Indeed, as the length of the ribbon is increased, the ratio of phonon contribution to thermal conductance to the electron contribution is reduced. At room temperature, when \( R_{\text{rms}} = 1.98 \text{ Å} \) and the chemical potential is pinned to the CNP, \( \sigma_{\text{el}}/\sigma_{\text{ph}} \) becomes 20.6, 2.3, and 0.3 for samples of lengths \( L = 0.25, 2.5, \) and 25 \( \mu \text{m} \), respectively. In Figure 7a,c, we plot the Seebeck coefficients at \( T = 300 \text{ K} \) for \( L = 61.5 \text{ nm} \) and \( L = 125 \text{ \mu m} \), respectively. Local extrema of Seebeck coefficients, when the chemical potential is close to \( \mu = 0.17 \text{ eV} \), are due to the rapid variation of the transmission function at the band edge, and \( R_{\text{rms}} = 1.98 \text{ Å} \) yields the highest magnitude for all samples at all temperatures considered. For \( L = 61.5 \text{ nm} \), \( ZT \) is always lower than \( 10^{-2} \). It increases with length and reaches the value of \( ZT = 0.41 \) for \( R_{\text{rms}} = 1.98 \text{ Å} \) when \( L = 125 \mu \text{m} \). Despite the fact that lattice thermal conductivity is lower for \( R_{\text{rms}} = 4.44 \text{ Å} \), such high \( ZT \) values are not observed for \( R_{\text{rms}} \) values larger than 1.98 Å. Again, this can be attributed to the suppressed electrical conductance for large \( R_{\text{rms}} \).

**CONCLUSION**

The electronic and thermal properties of GNRs are strongly dependent on the dimensions of the structure, edge termination/roughness, and lattice defect distribution. In this study, molecular dynamics and non-equilibrium Green’s function methods are utilized on GNRs of sizes up to micrometers in order to investigate the extent of these dependencies. Classical dynamics calculations show that decreasing the width, changing the termination of ribbons from zigzag to armchair, and roughening the edge all reduce the thermal conductivity due to an increase in the ratio of edge length to surface area. As this ratio increases, phonon edge scattering dominates the thermal behavior. Interestingly, the \( \kappa \) calculated for the roughest ribbon and the ones calculated for highest concentration of single vacancy, double vacancy, and Stone–Wales defects are all similar. Moreover, at these “extreme” concentration cases, \( \kappa \) behaves almost independent of the temperature, which is attributed to the defect-induced domination of elastic mean free paths over anharmonic mean free paths. Although the thermal conductivities of all the defected ribbons converged to similar values, the concentrations corresponding to these points are not all the same for internal defects. Single vacancies are more effective in decreasing \( \kappa \) compared to double vacancies and Stone–Wales defects. In fact, double vacancies and Stone–Wales defects do not show any quantitative difference.

Another dramatic difference between the effects of edge and bulk vacancies on the electronic conduction of ZGNRs suggests that bulk vacancies destroy the ballistic electronic transport properties of GNRs except when present within 7.5 Å of the edge. Despite the destruction of ballistic behavior by bulk defects, quantum conduction plateaus are still observable at low conductance values. Additionally, the electronic quality of ZGNRs with edge disorder can be preserved, provided that the edge roughness does not significantly breach the key 7.5 Å edge region. The weak dependence of electrical conduction on the edge roughness in ZGNRs is attributed to the fact that the electronic band within the first conduction plateau is only weakly dependent on the ribbon width, which is a characteristic of zigzag edge shape. Combined with
the suppressed lattice thermal conduction, edge-
disordered ZGNRs have significant thermoelectric po-
tential, while bulk defects suppress the thermoelectric quality.

METHODS

In order to calculate thermal conductivity, an accurate description of phonon dispersions, especially those of acoustic modes, of the considered material is extremely important as they strongly influence thermal transport properties. Lindsay et al. have recently shown that the original Tersoff and Brenner-type empirical interatomic potential parameters do not accurately reproduce the phonon dispersions or the group velocities of the three acoustic branches. They have also presented a reoptimized parameter set which, for suspended graphene and (10,10) single-wall carbon nanotubes, gives a κ in much better agreement with the experimental results. In this study, the reoptimized parameter set is employed to accurately represent the phonons in graphene-based systems.

Green–Kubo theory is a standard technique used in equilibrium molecular dynamics simulations for the determination of transport coefficients through the time-integrated autocorrelation functions relevant to the targeted transport property, as dictated by the fluctuation–dissipation theorem. The correlation function approach is equivalent to time evolution of various functions (e.g., mean square displacement to diffusion through Einstein relations). In particular, the thermal conductivity can be obtained from the equilibrium behavior of an energy moment vector, R

\[ \mathbf{R}(t) = \sum_i \mathbf{r}_i(t) \mathbf{i}_i(t) \]  

where \( \mathbf{i}_j \) is the energy content of atom \( i \). In a nonconductive system, this energy moment expression may be expressed as

\[ \mathbf{R}(t) = \sum_i \int_0^\infty f_i(r) v_i(r) dr \]

where \( f_i \) is a summation over all particles in the simulation cell as well as the images which form unique interaction groups (i.e., pairs for 2-body, triplets for 3-body, etc.). The force on particle \( i \) due to all unique interactions of \( i \) is represented by \( f_i, r_i \), and \( v_i \) are simply the position and velocity of the same particle. Using this definition, the thermal conductivity in a given direction, \( \kappa_{xy} \), is found via an equation akin to the Einstein diffusion expression

\[ \kappa_{xy} = \frac{1}{V_k B T} \lim_{T \to \infty} \frac{1}{2T} (\mathbf{R}_x(t) - \mathbf{R}_x(0)) (\mathbf{R}_y(t) - \mathbf{R}_y(0)) \]  

with \( T, k_b, \) and \( V \) being the temperature, Boltzmann constant, and volume, respectively.

Though Green–Kubo theory requires lengthy simulations to generate converged results, it provides the best representation of thermal conductivity, as the assumptions regarding phonon relaxation times, phonon velocities, and anharmonic effects required for other models are implicitly included in the temporal behavior of \( \mathbf{R}_x \). The simulations performed herein use the NVE ensemble and a time step of 1 fs, the optimum step that conserves energy and reliably converges \( \mathbf{R}_x \). Each data point for the thermal conductivity is obtained from the average of multiple simulations each lasting a minimum of 5 ns. A time scale on the order of a few nanoseconds is necessary to accurately average the vibrational processes that contribute to thermal conductivity. For the calculations with GNRs, we determine only the κ component along the direction of the ribbon length and define the volume as the surface area of the 2D GNR times the interplanar spacing of graphite.

For electronic transport calculations, a tight-binding (TB) model is employed together with non-equilibrium Green’s functions. The tight-binding Hamiltonian is written as

\[ H = -t \sum_{\langle i,j \rangle} (c_i^\dagger c_j + c_j^\dagger c_i) + \mathcal{H}_C \]  

where \( t = 2.7 \text{ eV} \) and \( c_i^\dagger (c_i) \) is the electron creation (annihilation) operator at site \( i \), and the summation runs over the first nearest neighbors. The TB Hamiltonian is known to yield results in agreement with first-principles density functional theory (DFT) calculations for graphene in both one and two dimensions and also in the presence of vacancies. We determined the electronic band structure for pristine ZGNR (70) as well as defective ZGNRs. Here, 70 is the number of zigzag chains in the transverse direction, and it corresponds to a width of 15 nm. Pristine ZGNR is a zero gap semiconductor independent of its width with a high density of states around the charge neutrality point (CNP). The reservoirs are modeled with semi-infinite pristine GNRs coupled to the central region from left and right, and the electronic conductance is calculated as

\[ \sigma(\mu, T) = \left. -\frac{2e^2}{h} \int_{-\infty}^{\infty} dE \right| \frac{\partial \Gamma(\mu, T)}{\partial E} \]  

with \( \Gamma(\mu, T) \) being the Fermi distribution function, \( \mu \) is the chemical potential, \( T \) is temperature and \( \sigma \) is the transmission coefficient. Here \( \Gamma_{(10)} \) stands for the transmission due to coupling to the left (right) reservoir, \( \Gamma_{(10)} \) is the retarded (advanced) GF of the central region. Long ribbons are calculated using the recursion scheme. We carry out calculations for 25 different realizations of disorder and perform ensemble averages. Onsager coefficients are calculated using the functions \( L_{(2)}(\mu, T) = \int dE \mu (\mathcal{E}(\mu, T)) \mathcal{G}_{(2)}(\mathcal{E}(\mu, T)) \), the temperature-dependent electrical conductance is defined as \( \sigma(\mu, T) = (2e^2/h)\mu \rho_0 \), and the Seebeck coefficient can be obtained with \( \sigma(\mu, T) = (1/e)T/L_1 \rho_0 \). The electron and phonon contributions to thermal conductance are given with \( \sigma_{(2)}(\mu, T) = (2/h)T(L_2 - L_1) \rho_0 \) and \( \sigma_{(ph)} = \kappa(A/L) \), respectively. Here, \( A \) is the cross section area, \( L \) is length of the ribbon, and \( \kappa \) is the lattice thermal conductivity. Thermoelectric figure of merit is defined as

\[ ZT = \frac{\sigma_\mu^2 T}{\kappa_{ph} + \kappa_{el}} \]  

In this study, we employed both classical dynamics and tight-binding model to rough ribbons which are created by randomly but continuously varying the edge profile between predefined limits. The distance between the limits, consequently, determines the roughness for an edge. In defining the roughness for the ribbons, we used a common root mean squared parameter, \( \rho_{rms} \). Briefly, \( \rho_{rms} \) is the standard deviation of the positions of atoms at the edge from the mean of the whole edge. Since there are two edges, the total roughness is the average of these two.

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REFERENCES AND NOTES


