Size and Chirality Dependence on Thermoelectric Properties of Graphene Nanoribbons

Wen Huang and Gengchiau Liang[#]

Department of Electrical and Computer Engineering, National University of Singapore, Singapore; Phone: +65-6516-2898 #E-mail: elelg@nus.edu.sg

1. Introduction

Graphene, a single layer of graphite, has attracted great attention due to its prominent physical properties and potential applications on various devices. [1] Graphene nanoribbons (GNRs), nanometer-sized graphene strips, are also widely considered as potential channel materials for nanoelectronic devices. GNRs have different electrical properties compared to graphene sheets due to quantum confinement and different edge terminations [2-4]. Due to the world's increasing demand for energy and the challenge of environmental problems, thermoelectric materials, as alternative clean energy sources, have received considerable attention over the years. Thermoelectric effects can be used in cooling applications for electrical devices and to generate energy from waste heat. The thermoelectric properties on 2D graphene have been well studied theoretically and experimentally [5,6]. Although it is discovered that nanostructure can improve the thermoelectric performance [7], there is not enough information on the thermoelectric performance on quasi-1D GNRs, especially its geometry dependence.

In this work, we investigate the effects of size and chirality on thermoelectric properties of GNR. We use a semi-classical ballistic transport approach based on intrinsic material properties without consideration of scattering and edge effects. Electron and phonon energy dispersion relations are calculated using tight-binding and force constant model, respectively [8,9]. Then, the carrier transport and thermoelectric properties are calculated based on ballistic Boltzmann transport equation [10], and the key equations used in this work are listed below.

$$i_m^p = \int_{-\infty}^{\infty} dE \vec{v}^p \times DOS^p(E) \times (f_1 - f_2) \times (E - \mu)^m$$
(1)

$$I_m = \frac{d\sum_{all \ subband \ p} i_m^p}{dV} \tag{2}$$

$$G = qI_0 \tag{3}$$

$$S = \frac{I_1}{qTI_0} \tag{4}$$

$$\kappa_{e} = \frac{1}{T} (I_{2} - \frac{I_{1}^{2}}{I_{0}})$$
(5)

$$I_{ph} = \frac{2}{h} \sum \Delta E_{ph,k} \times E_{ph,k} \times (n_{B+} - n_{B-})$$
(6)

$$\kappa_{ph} = \frac{I_{ph}}{\Delta T} \tag{7}$$

where \overline{v}^{p} represents the average group velocity, $DOS^{p}(E)$ stands for the density of state, with the superscript *p* indicat-



Fig 1. (a) Structure of AGNR, width d = 1 nm. (b) ZT as a function of reduced Fermi level for AGNR with different d, 1(blue), 2.2(green), 4(red), 7(light blue) and 10(purple) nm. (c) S and G as a function of reduced Fermi level for for AGNR with different d. (1 and 2.2 nm lines are overlapped) (d) $\kappa_{ph} + \kappa_e$ and κ_{ph} / κ_e ratio as a function of reduced Fermi level for for AGNR with different d.

ing contribution from the *p*th subband based on the E-k relations. f_1 (f_2) and n_{B+} (n_{B-}) are the Fermi-Dirac distribution and Bose-Einstein distribution at the end reservoir. Therefore, the dimensionless figure of merit can be represented as

$$ZT = \frac{S^2 GT}{\kappa_{ph} + \kappa_e} \tag{8}$$

where S, G, T and κ_{ph} , κ_e are the Seebeck coefficient, electrical conductance, absolute temperature, thermal conductance by phonon or electron contribution, respectively.

2. Results and Discussion

Firstly, we investigate the thermoelectric properties of

perfect armchair GNR (AGNR) with width (d) of 1, 2.2, 4, 7 and 10 nm as a function of reduced Fermi level, $\eta_F =$ $(E_F - \varepsilon_I)/k_BT$, where ε_I is the first subband edge, i.e., the lowest conduction band or the highest valence band edge of AGNRs. In this work, we select all GNRs from the same family of 3p which exhibits semiconducting behavior. As shown in Fig. 1(b), ZT peak values (at T = 300 K) of AGNRs with different widths occur around $\eta_F = 0$ and monotonically increase as d of AGNRs decreases. It indicates that the nano-scale GNRs have better thermal properties than GNRs with larger widths. To understand the details of these phenomena, we investigate the individual contribution from electrons and phonons. As shown in Fig. 1(c), as η_F increases, S decreases and G increases. It is because that more subbands are available for electronic conduction. However, around $\eta_F = 0$, these two parameters remain same. Therefore, it indicates the enhancement of ZT is contributed by the thermal conductance. As show in Fig. 1(d), GNRs with larger width have the larger thermal conductance since more phonon vibration modes are involved in energy transport. As a result, ZT peak values of GNR with smaller widths are higher than those of larger widths. Furthermore, we investigate the details of the thermal conductance contributed by electrons (κ_e) and phonons (κ_{ph}). It is well-known that for bulk, i.e. GNR with large width, thermal conductance is dominated by phonon. However, as d decreases, electrons also will play an important role in heat transport as shown in Fig. 1(d).

Next, we investigate the chirality dependence on the thermoelectric properties of GNRs. Two typical edge types, armchair ($\alpha = 0^{\circ}$) and zigzag ($\alpha = 30^{\circ}$) are shown in Fig. 2(a), and we also study other edge types with α between 0° and 30°. Fig. 2(b) shows that the peak ZT values are dependent on size and chirality angle. At larger sizes, d = 4, 7and 10 nm, ZT values are zeros for GNR with different α except for 0° (AGNR). The reason lies in their electronic band structures. For cases with zero ZT, zero bandgap (E_{φ}) and metallic behavior are exhibited as shown in Fig. 2(c). However, when the size is shrunk down, their behavior has changed. At d = 1 nm, GNRs with $\alpha = 5^{\circ}$, 7° , 11° , and 16° have larger peak ZT values than that of AGNR, while at d =2.2 nm, GNR with $\alpha = 5^{\circ}$, and 7° also have larger peak ZT values than that of AGNR, which means they exhibit semiconducting behavior. As mentioned above, for AGNR with different d, κ_{ph} dominates the trend of ZT. However, this is not the case for GNRs with other chirality angles. Although for larger width cases, κ_{ph} of GNR with other α is comparable to that of AGNR as shown in Fig. 2(d), the peak ZT values are still zero due to the zero bandgap.

The peak ZT values obtained are not very high without considering edge effects. Other groups have shown that ZT can be improved by counting in defects, edge roughness and disorder [11,12]. However, the thermal conductance we obtained in ballistic model is enough to make GNR as a potential candidate for energy management and cooling device application.

3. Conclusions

In summary, we have studied the thermoelectric properties of GNRs in terms of Seebeck coefficient, electrical



Fig. 2 (a) GNR structure with different chirality angles (α). (b) ZT, (c) energy gap, (d) κ_{ph} as a function of chirality angle.

conductance, thermal conductance and figure of merit. These properties are investigated to be dependent on GNR geometry. The simulation results show that as the size is decreasing, ZT is increasing. Moreover, chirality plays an important role on thermoelectric properties of GNR. Furthermore, the smooth GNRs might not be the good thermoelectric materials due to low ZT caused by the high thermal conductance. However, this property can be applied to the cooling devices.

Acknowledgements

This work was supported by MOE, Singapore under Grant Nos. R263000578112.

References

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).
- [2] X. Li, X. Wang, L. Zhang, S. Lee, and H. Dai, Science 319, 1229 (2008).
- [3] A. K. Geim, and K. S. Novoselov, Nature Mater. 6, 183 (2007).
 [4] C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass,
- A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, Science 312, 1191 (2006).
- [5] Y. M. Zuev, W. Chang, and P. Kim, Phys. Rev. Lett. 102, 096807 (2009).
- [6] T. Lofwander and M. Fogelstrom, Phys. Rev. B 76, 193401 (2007).
- [7] Mildred S. Dresselhaus, Gang Chen, Ming Y. Tang, Ronggui Yang, Hohyun Lee, Dezhi Wang, Zhifeng Ren, Jean-Pierre Fleurial, and Pawan Gogna, "New Directions
- for Low-Dimensional Thermoelectric Materials" Adv. Mater 19, 1043 (2007) [8] S. Datta, Quantum transport: atom to transistor, Cambridge University Press (2005).

[10] T. Markussen, A. P. Jauho, and M. Brandbyge, Phys. Rev. B 79, 035415 (2009).

[12] H. Sevincli, and G. Cuniberti, Phys. Rev. B 81, 113401 (2010).

^[9] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Physical properties of carbon nanotubes, World Scientific Publishing Company (1998).

^[11] X. Ni, G. Liang, J.- S. Wang, and B. W. Li, Appl. Phys. Lett. 95, 192112 (2009).