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Optimization of thermoelectric power factor and deviation from Mott's formula of edge-disordered semiconducting graphene nanoribbons

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ABSTRACT

The room-temperature thermoelectric properties of semiconducting graphene nanoribbons (GNRs) with edge disorder were computationally investigated. The thermoelectric power factor (*PF*) of edge-disordered GNRs (ED-GNRs) can be maximized by adjusting the ribbon length, L_g. For example, the *PF* of armchair-type ED-GNRs with an edge disorder concentration C_d of 5% has a maximum value of 16.2 mW/(m K^2) at L_g = 146 nm and a chemical potential μ of −0.6 eV. The appearance of the maximum *PF* can be understood by a crossover phenomenon where electric conduction in an ED-GNR gradually changes from ballistic transport to Anderson localization as L_g increases. In addition, Mott's formula, which is well known as the relation between the Seebeck coefficient and electrical conductance, could not be applied to ED-GNRs within the Anderson localization regime.

1. Introduction

Thermoelectric materials are expected to be applied to self-sustaining power sources for various wearable devices because they can directly convert unused thermal energy into electrical energy. In 1993, Hicks and Dresselhaus theoretically proposed that the thermoelectric efficiency of materials can be significantly enhanced by processing them into one-dimensional nanowire shapes [1]. As such, diverse nanowires with high thermoelectric performance have been discovered thus far [2–6]. The present challenge in this field is the design of eco-friendly and flexible thermoelectric nanomaterials that can operate on curved surfaces such as the human body.

Graphene is a practical thermoelectric nanomaterial that consists of a two-dimensional honeycomb lattice of carbon atoms [7]. Graphene nanoribbons (GNRs) are mono-layered graphene in the shape of a nanometer-width ribbon. In addition to being non-toxic and flexible, GNRs have high thermoelectric power exceeding that of graphene due to a low-dimensional effect, as proposed by Hicks and Dresselhaus [8,9].

However, in contrast with high thermoelectric power, the thermoelectric efficiency of GNRs suffers due to their high thermal conductivity which is comparable to that of diamond and carbon nanotubes [10]. It is therefore desirable to develop techniques to reduce the thermal conductivity of GNRs without a reduction in their thermoelectric power. As such a technique, here we consider the introduction of edge disorder to GNRs, because even a small amount of edge disorder is known to dramatically suppress the thermal conductivity of GNRs [11].

We have previously reported that metallic GNRs with a zigzag-type edge (ZGNRs) retain sufficient thermoelectric power after the introduction of edge disorder. In addition, the thermoelectric power of edge-disordered ZGNRs (ED-ZGNRs) could be optimized by adjustment of the length of the disordered region; therefore, we have proposed that ED-ZGNRs are a promising candidate for thermoelectric applications [12].

There is another type of GNR edge structure called an armchair-type edge (AGNR), which, unlike ZGNRs, can be either metallic or semiconducting, depending on their width [13]. Although semiconducting AGNRs are a potential candidate for high-performance thermoelectric nanomaterials, the influence of edge disorder on their thermoelectric properties has yet to be elucidated. Therefore,

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here we computationally investigate the influence of edge disorder on the thermoelectric properties of semiconducting AGNRs at room temperature (300 K).

2. Landauer theory

In Landauer theory, electric current I, is expressed by:

$$I = -\frac{2q}{h}\int_{-\infty}^{\infty} \zeta(\varepsilon)[f(\varepsilon,\mu_L,T_L) - f(\varepsilon,\mu_R,T_R)]d\varepsilon, \quad (1)$$

where q is the charge of an electron, h is Planck's constant, $\zeta(\varepsilon)$ is the transmission function of an electron with energy ε, and f is the Fermi Dirac distribution function of a left (right) lead at chemical potential $\mu_{L(R)}$ and temperature $T_{L(R)}$ [14]. In this research, the Fermi energy was set as zero ($\varepsilon = 0$).

In the case of small differences for both chemical potential and temperature, Eq. (1) is approximated as:

$$\Delta I \approx \Delta\mu\frac{-2q}{h}\int_{-\infty}^{\infty}\zeta(\varepsilon)\frac{\partial f}{\partial\mu}d\varepsilon + \Delta T\frac{-2q}{h}\int_{-\infty}^{\infty}\zeta(\varepsilon)\frac{\partial f}{\partial T}d\varepsilon, \quad (2)$$

where $\Delta\mu = \mu_L - \mu_R$ and $\Delta T = T_L - T_R$. Using Eq. (2), the electrical conductance G and Seebeck coefficient S of materials can be expressed, respectively, as:

$$G \equiv \lim_{\Delta V\to 0}\left(\frac{\Delta I}{\Delta V}\right)_{\Delta T=0} = q^2K_0, \quad (3)$$

$$S \equiv \lim_{\Delta T\to 0}\left(\frac{\Delta V}{\Delta T}\right)_{\Delta I=0} = -\frac{1}{qTK_0}\frac{K_1}{}, \quad (4)$$

where the intermediate function K_n is defined as:

$$K_n \equiv \frac{2}{h}\int_{-\infty}^{\infty}\zeta(\varepsilon)\left(-\frac{\partial f}{\partial\varepsilon}\right)(\varepsilon-\mu)^n d\varepsilon. \quad (5)$$

The maximum thermoelectric power is determined by the thermoelectric power factor PF, which is defined by:

$$PF = \sigma S^2. \quad (6)$$

Here, σ is the electrical conductivity, which is related to G via

$$\sigma = \frac{L_g}{A}G, \quad (7)$$

where L_g is the length of the disordered region of a GNR (see Section 3) and A is the cross-section of a GNR, defined as $W \times d$ (W: GNR width, d: GNR thickness). A GNR thickness of $d = 0.335$ nm was adopted, which corresponds to twice the van der Waals radius of a carbon atom.

3. Simulation model and method

Simulation models were constructed from three regions: a central scattering region, and left and right leads. The scattering region comprises an edge-disordered AGNR (ED-AGNR) with an averaged width W, of 1.67 nm and the length of the disordered region L_g, as shown in Fig. 1. The left and right leads are pristine AGNRs with $W = 1.67$ nm and a semi-infinite ribbon length. Each edge carbon atom is terminated by a hydrogen atom. In the present study, ED-AGNRs with various L_g between 10 and 198 nm were examined.

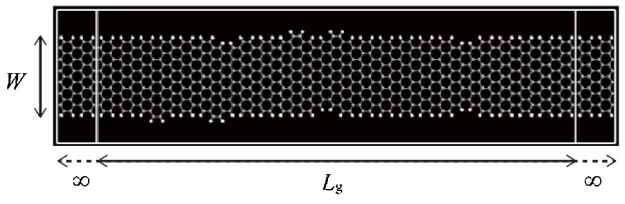

Fig. 1. Scattering region sandwiched between two leads. The scattering region comprises an ED-AGNR with an averaged width W and the length of the disordered region, L_g. Gray and white balls denote carbon and hydrogen atoms, respectively.

The edge disorder, which was modeled by the addition and removal of carbon atoms at the edges, was taken to be randomly distributed in the central region, as shown in Fig. 1. It was assumed that the numbers of carbon atoms added and removed (N_a and N_r, respectively) were the same, *i.e.*, $N_a = N_r$. The edge disorder concentration C_d, was defined as:

$$C_d = \frac{N_a + N_r}{N_{edge}}. \quad (8)$$

Here, N_{edge} is the total number of edge carbon atoms.

The Atomistix ToolKit ver. 2014.2 [15] was used to compute the electron transmission function $\zeta(\varepsilon)$ of an each ED-AGNR sandwiched between two pristine AGNR leads with semi-infinite length. The computation was based on the non-equilibrium Green's function (NEGF) method combined with the tight-binding approximation. The transfer integrals between each pair of $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals of the carbon atoms were obtained by the Slater-Koster parameter [16].

Using Eqs. (3)–(7), the electrical conductivity σ, Seebeck coefficient S, and thermoelectric power factor PF were calculated for 1000 ED-AGNRs with different configurations of edge disorder for fixed L_g and C_d. The averaged conductivity $<\sigma>$, Seebeck coefficient $<S>$, and power factor $<PF>$ were then estimated by averaging σ, S, and PF for 1000 samples. All simulations were performed at room temperature (300 K).

4. Simulation results

4.1. Thermoelectric power factor

Fig. 2 presents the chemical potential μ dependence of the averaged thermoelectric power factors $<PF>$ for ED-AGNRs with various C_d from 0% to 20% at $L_g = 10$ nm. Fig. 2 shows that the PF for pristine AGNRs with $C_d = 0\%$ (solid line) has 4 sharp peaks at −0.33, +0.33, −0.6 and +0.64 eV, which are located in the vicinity of the energy-band edges. The PF values at the first peaks of −0.33 and +0.33 eV are approximately 13 mW/(m K^2), and PF at the second peaks of −0.6 and +0.64 eV are approximately 3.4 mW/(m K^2).

As shown in Fig. 2, $<PF>$ at the second peaks are not strongly reduced by the introduction of edge disorder, whereas $<PF>$ at the

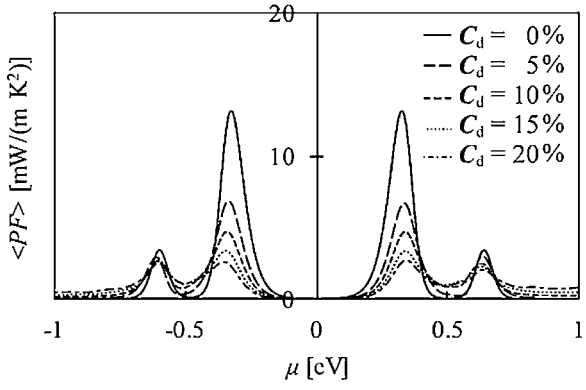

Fig. 2. Dependence of on $<PF>$ μ for ED-AGNRs with various C_d at $L_g = 10$ nm.