Thermoelectric properties of one-dimensional graphene antidot arrays

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Abstract

We investigate the thermoelectric properties of one-dimensional (1D) graphene antidot arrays by nonequilibrium Green’s function method. We show that by introducing antidots to the pristine graphene nanoribbon the thermal conductance can be reduced greatly while keeping the power factor still high, thus leading to an enhanced thermoelectric figure of merit (ZT). Our numerical results indicate that ZT values of 1D antidot graphene arrays can be up to unity, which means the 1D graphene antidot arrays may be promising for thermoelectric applications.

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1. Introduction

Recently, graphene has drawn extensive attention due to its exceptional properties, such as high electron mobility [1,2] and the tunable band gap and magnetic properties by the size and edge chirality [3–5]. These unusual electronic properties could have many applications, particularly in nanoelectronic devices [6]. Meanwhile, thermoelectric properties of graphene have also attracted increased interest, since it can convert heat to electricity or vice versa. The efficiency of a thermoelectric device is usually characterized by the figure of merit $ZT = S^2T/\lambda$, where $S$ is the Seebeck coefficient (or thermopower), $T$ is the electronic conductance, $T$ is the temperature, and $\lambda$ is the total thermal conductance including contributions from both phonons and electrons. The ideal thermoelectric material is the so-called “phonon-glass–electron-crystal” with a high thermopower $S$ and a low thermal conductance $\lambda$. Indeed a high thermopower value up to 80 $\mu$V/K was reported for graphene [7,8]. Then the natural question is whether we can design specific structures so that the thermal conductance is degraded while the electronic conductance and the thermopower are still high. In this context, different structures of graphene have been examined, including various graphene nanoribbons (GNRs) [9–13], graphene quantum dots [14], graphene junctions and chevron-type structures [15], etc. It is noteworthy that $ZT$ of zigzag GNRs with edge disorder can exceed 3 [13].

Very recently, graphene antidot lattices have attracted a lot of interests [16–21]. This is partially due to the fact that, by making an array of holes (antidots) in the graphene layer, a band gap (which is necessary for application of graphene in transistor architectures) could be created [17,18]. The size of the gap can be tuned by varying the lattice geometry, that is, the antidot size and separation. This structure has also been the subject to recent experimental research, and indeed antidot lattices with different geometries have been fabricated using different techniques [22–25]. Further, in recent works [26,27], thermoelectric properties of two-dimensional graphene antidot lattices have also been studied with $ZT$ being up to 0.3.

In this Letter we consider the thermoelectric properties of 1D graphene antidot arrays with zigzag edges since it was demonstrated that reduced dimensionality could lead to enhanced $ZT$ values [28]. We will show that, by introducing antidots to the zigzag graphene nanoribbon, the thermal conductance can be reduced largely without negatively affecting the power factor $(S^2\lambda)$ and, thus, the thermoelectric figure of merit $ZT$ can be enhanced. With increasing sizes of antidots, $ZT$ can be increased further to about one, which means the 1D graphene antidot arrays may be promising for thermoelectric applications.
an increase of the hopping integral between carbon atoms along model also applies to 1D antidot arrays. In realistic graphene sam-
tidot is non-passivated antidot lattices are much similar[20]. Therefore, antidot lattices, the electronic structures of the passivationed and close to the Fermi level[20]. Thus we may expect that the TB obtained from density functional theory (DFT), especially for bands should be pointed out that, within the TB model (1) with nearest-neighbor hopping, spin polarization[30,31] effect is not considered while for this effect is not taken into account in the present work. Finally, it should be pointed out, that within the TB model (1) with nearest-neighbor hopping, spin polarization[30,31] effect is not considered as we focus on the charge transport. To consider this effect, one may need to take into account the electron–electron interaction that changes the electronic structures of nanoribbons slightly[31].

Within the TB model, we can calculate the electronic current using the standard nonequilibrium Green's function (NEGF) formal-

\[ I = \frac{2e}{h} \int dE T_{e}(E) \left[ f(E, \mu_{L}) - f(E, \mu_{R}) \right], \]

where \( T_{e}(E) \) is the electron transmission, and \( f(E, \mu_{L,R}) = 1/(\exp(E - \mu_{L,R})/k_{B}T) + 1 \) is the Fermi–Dirac distribution function in the left and right leads with chemical potentials \( \mu_{L,R} \). The electronic conductance is

\[ G_{e}(\mu) = \frac{2e^{2}}{h} \int dE T_{e}(E) \left( -\frac{\partial f(E, \mu)}{\partial E} \right) = e^{2}L_{0}, \]

where the function \( L_{0}(\mu) \) is defined as

\[ L_{0}(\mu) = \frac{2}{h} \int dE T_{e}(E)(E - \mu)^{m} \left( -\frac{\partial f(E, \mu)}{\partial E} \right). \]

The thermopower \( S \) and electron thermal conductance \( \lambda_{e} \) can be shown to be \( S = -\frac{1}{\tau} \left( \frac{L_{1}}{L_{2}} \right) \) and \( \lambda_{e} = \frac{1}{\tau} \left( \frac{L_{2}}{L_{1}} \right) \), respectively.

The phonon transport is modeled by a fourth-nearest-neighbor force constant (4NNFC) model, which yields phonon dispersions in agreement with first-principles results for graphene and carbon nanotubes[15,34]. The force constants used in our work are adopted from Ref. [34]. These parameters yields a considerable improvement in the overall phonon dispersion of graphene as compared to the parameters given in Ref. [35]. In a recent work[15], these parameters were tested for nanoribbons, where the results obtained are consistent with first-principles calculations. Within this model, the phonon thermal current can then be calculated from the phonon transmission function \( T_{ph} \) as

\[ J_{ph}(T) = \frac{h}{2\pi} \int d\omega \omega T_{ph}(\omega) \left[ n_{B}(T_{L}) - n_{B}(T_{R}) \right], \]

where \( n_{B}(T_{L,R}) = (e^{\hbar\omega/k_{B}T_{L,R}} - 1)^{-1} \) is the Bose–Einstein distribution and \( T_{L,R} \) is the left (right) bath temperature. In the linear response regime, the phonon thermal conductance is then

\[ \lambda_{ph}(T) = \frac{\hbar^{2}}{2\pi k_{B} T_{L} T_{R}} \int d\omega \omega^{2} T_{ph}(\omega) \left( e^{\hbar\omega/k_{B}T} - 1 \right)^{2}. \]

Again, we do not consider the hydrogen-passivation here. Actually, it was shown recently that passivation could reduce the thermal conductance of a ribbon[37], which is beneficial to the thermoelectric properties.

Using the above equations, the thermoelectric figure of merit of a material can be expressed as

\[ ZT = \frac{S^{2}G_{e}T}{\lambda_{ph} + \lambda_{e}}. \]

In our simulations, we treat both phonons and electrons as free particles, and thus the phonon contribution to thermoelectric power caused by phonon-drag is naturally ignored. Indeed, recent studies show that, at temperatures \( T > 10 \) K, the contribution to thermoelectric power mainly comes from diffusive processes and the phonon-drag effect can be ignored[38,39].

3. Results and discussions

We first consider the heat transport properties in graphene antidot arrays. Fig. 2(a) shows the phonon thermal conductance of finite antidot arrays, where antidots are located at the middle of the
nanoribbons. By finite antidot arrays, we mean that the two leads are semi-infinite pristine graphene nanoribbons. As the number of antidots increases, the thermal conductance at a given temperature reduces rapidly. When the number of antidots is \(N=3\), the thermal conductance approaches that of an infinite antidot array. The thermal conductance of the infinite antidot array is much smaller than that of the corresponding pristine nanoribbon. For example, at \(T=300\) K the thermal conductance of the infinite antidot array is about \(18 \times 10^{-10}\) W/K while the thermal conductance of the pristine nanoribbon is about \(33 \times 10^{-10}\) W/K. The rapid convergence of thermal conductance with increasing \(N\) is also reflected in the phonon transmission, which is shown in Fig. 2(b). From Fig. 2(b), we can see that phonon transmission of the pristine nanoribbon is much larger than those of the antidot arrays for most energy values except very low energies, which means that low energy phonons (with long wavelengths) can be hardly scattered by the antidots when the antidot size is much smaller than the wavelengths of low energy phonons. Since the phonon band structure (not shown here) of the infinite antidot array is much complex, the transmission of the infinite antidot array oscillates around that of the nanoribbon with three antidots, thus leading to very close thermal conductances of these two nanoribbons.

Fig. 3 shows the phonon thermal conductances of three nanoribbons when the radii of antidots in the middle are different. As the radii of antidots increase, the thermal conductance \(\lambda_{\text{ph}}\) reduces, which indicates that phonons are scattered more effectively by large antidots. In fact, the phonon thermal conductance is limited by the narrowest part (ribbon width minus antidot diameter) of antidot array that determines the number of channels of phonon transport. This actually offers a possible way to tailor the thermal conductance of graphene nanoribbons by controlling the sizes of antidots. In the inset of Fig. 3, we show the thermal conductance when the distances between antidots are changed while keeping the sizes fixed. We can see that thermal conductance decreases slightly when the distance between antidots is reduced. This is reminiscent of the fact that impurity aggregates may scatter phonons much more efficiently than if they were acting separately [40,41]. Furthermore, it is worthy to point out that, from our simulations (not shown here), the thermal conductance only slightly depends on the relative positions of antidots to the edge \(d'\).

Now we begin to study the thermoelectric properties of the antidot arrays. Fig. 4(a) presents the Seebeck coefficient \(S\) and the electron transmission of an infinite antidot array. The Seebeck coefficient will normally display a peak value around the point, where a sharp change of electron transmission occurs [42]. Thus depending on the electron transmission variation, the Seebeck coefficient displays several peak values of order 150–500 \(\mu \text{V/K}\) which is similar to those obtained for other graphene systems [12,26]. The magnitude of the two main peaks \(S\) values, due to a change of electron transmission occurring at \(E=0.45\) eV and \(E=0.88\) eV, is about 500 \(\mu \text{V/K}\). This leads to two peak \(ZT\) values of about 0.65 around \(\mu = 0.5\) eV and \(\mu = 0.83\) eV as shown in Fig. 4(b). The peak \(ZT\) value around \(\mu = 0.5\) eV changes around 0.6 with temperature [see inset of Fig. 4(b)]. Fig. 5 shows the electronic structures and thermoelectric properties of the antidot arrays when the distance \(d'\) of the antidots to the upper edge of the ribbon is changed to \(d'=4a_0\) and \(d'=5.5a_0\). As the particle–hole symmetry is pre-
Fig. 5. (Color online.) Thermoelectric properties of an infinite antidot array with \( r = 2a_0 \) and \( d = 5\sqrt{3}a_0 \) when the distances of the antidots to the upper edge are \( d' = 4a_0 \) and \( d' = 5.5a_0 \), respectively. (a) and (b) show the electronic structures, while (c) and (d) show \( ZT \) and the Seebeck coefficient at \( T = 300 \) K.

Fig. 6. (Color online.) (a) Maximal \( ZT \) value of an infinite antidot array at \( T = 300 \) K as a function of the antidot size. The antidots are separated by two hexagons in between (see Fig. 1). (b) and (c) plot the corresponding \( S^2G_e \), \( \lambda_e \), and \( \lambda_{ph} \).

Fig. 7. (Color online.) (a) Maximal \( ZT \) value for infinite antidot arrays at \( T = 300 \) K as a function of the distance between antidots. Here \( d = \sqrt{3}a_0 \) is the lattice constant. \( r = 3.6a_0 \). (b) and (c) plot the corresponding \( S^2G_e \) and the thermal conductance when \( ZT \) takes the maximal values. We can observe that, by introducing antidots to the pristine nanoribbon, \( S^2G_e \) does not degrade, or even increases a little when \( r = 2a_0 \) or \( r = 3.6a_0 \). However, the thermal conductances (from both phonons and electrons) decreases greatly, thus leading to enhanced thermoelectric figure of merit. In Fig. 6, the antidots have zigzag edges except those with \( r = 4.35a_0 \), and thus it is likely that the edge shape of the antidots may not affect the maximal \( ZT \) value much.

In Fig. 6(a), we present the maximal \( ZT \) values (\( ZT_{\text{max}} \)) of several infinite antidot arrays for \( \mu \) in [0, 1] eV when the sizes of antidots are changed. It is clear that the maximal \( ZT \) values roughly increase with increasing antidot sizes. In the pristine nanoribbon (\( r = 0 \)), the maximal \( ZT \) value is about 0.1, while it increases up to about 1.2 when \( r = 5a_0 \). The maximal \( ZT \) value of the antidot array is much larger than that of the pristine nanoribbon (about 0.1). The lower \( ZT \) values of the pristine nanoribbon can be ascribed to large thermal conductance contributed by both phonons and electrons as can be seen from Fig. 6(c). Figs. 6(b) and (c) plot the corresponding \( S^2G_e \) and the thermal conductance when \( ZT \) takes the maximal values. We can observe that, by introducing antidots to the pristine nanoribbon, \( S^2G_e \) does not degrade, or even increases a little when \( r = 2a_0 \) or \( r = 3.6a_0 \). However, the thermal conductances (from both phonons and electrons) decreases greatly, thus leading to enhanced thermoelectric figure of merit. In Fig. 6, the antidots have zigzag edges except those with \( r = 4.35a_0 \), and thus it is likely that the edge shape of the antidots may not affect the maximal \( ZT \) value much.

In Fig. 7(a), we present the maximal \( ZT \) values (\( ZT_{\text{max}} \)) of several infinite antidot arrays, where we keep the sizes of antidots fixed while changing the distances between the antidots. At \( d = 8\sqrt{3}a_0 \equiv 8a_0 \), \( S^2G_e \) is larger as compared to other distances, leading to a higher maximal \( ZT \). For \( d < 8a_0 \), \( ZT \) slightly increases with increasing \( d \). Further, it is interesting to note that the thermal conductances at the maximal \( ZT \) points are dominated by phonons as indicated by Fig. 7(c) [or Fig. 6(c)].
Finally, we consider the thermoelectric properties of finite antidot arrays, which are shown in Fig. 8. From Fig. 8(a), we see that the $ZT$ value converges to a stable value as the number of antidots in nanoribbon increases. However, the converged peak $ZT$ values of the finite arrays are smaller than that of the infinite antidot array. As we have already demonstrated that the phonon thermal conductances in finite antidot arrays converge fast to the limit value of the infinite array with increasing number of antidots, then the reduction of peak $ZT$ values in finite arrays is naturally caused by the decrease of $S^2G_v$ as shown in Fig. 8(b). This is mainly due to electron scattering at the interfaces between the pristine leads and the central region.

4. Conclusion

In summary, we have investigated the thermoelectric properties of 1D graphene antidot arrays with zigzag edges. We have shown that for finite antidot arrays the phonon thermal conductance converges rapidly to the value of an infinite antidot array as the number of antidots increases. The phonon thermal conductance of antidot arrays is much lower than that of the pristine graphene nanoribbons. By increasing the sizes of antidots, the thermal conductance can be reduced further, thus leading to an enhanced thermoelectric figure of merit. Indeed, our results indicate that $ZT$ values of 1D antidot arrays can be up to or exceed unity. This indicates that the 1D antidot arrays may be promising for thermoelectric applications. To fabricate such structures, possibly one could first fabricate a 2D graphene nanomesh, and then sculpt it to a ribbon shape [43].

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References