

# High thermoelectric figure of merit in devices made of vertically stacked graphene layers

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**Abstract**— We study the thermoelectric properties of devices made of two partially overlapped graphene sheets. As a consequence of the weak van der Waals interactions between graphene layers, it is shown that the phonon conduction in these junctions is strongly reduced compared to that of single graphene layer structures. In contrast, their electrical conductance is more weakly affected. We hence demonstrate that the thermoelectric figure of merit can reach values higher than 1 at room temperature in graphene materials having the advantage of offering either a bandgap or a conduction gap. We consider in particular the cases of stacks of armchair graphene nanoribbons, misoriented graphene nanoribbons and graphene nanomeshes. For the latter device, a figure of merit of 1.8 is obtained at room temperature and reaches even 3.2 at 600K. The vertical design of graphene layers thus appears as an efficient way to achieve high thermoelectric efficiency in graphene devices.

**Keywords**—graphene; thermoelectrics; Green's functions

## I. INTRODUCTION

The thermoelectric effect enables direct conversion of a temperature difference into an electric voltage and vice versa, and provides a viable route for electrical power generation from waste heat. In principle, to achieve high thermoelectric efficiency, it is needed to suppress thermal conductance while keeping high electrical conductance and thermoelectric power. It has been shown in the literature that this issue is usually difficult to solve in conventional bulk materials, however, the use of low dimensional materials and/or nanostructuring could be promising options [1], [2].

Actually, to make graphene a good thermoelectric material, we have two important issues to overcome. The first one is its gapless character, which makes it difficult to separate the opposite contributions of electrons and holes to the thermoelectric power  $S$ , leading to a small value of  $S < 100 \mu\text{V}/\text{K}$  in pristine graphene [6]. The second one is its high thermal conductivity that leads to low thermoelectric efficiency in graphene devices. It has been suggested to solve the first issue by bandgap engineering, e.g., with graphene nanoribbons, graphene nanomesh lattices, hybrid graphene/hexagonal BN structures etc... [3]. For the second issue, other approaches as edge roughness, defect or isotope engineering, together with nanostructuring in nanohole lattices, have been demonstrated as promising options.

The thermal properties of graphite and graphene multilayer systems are highly anisotropic [7], [8]. While the thermal conductance along the in-plane direction is high in graphite [4], it is hundreds of times smaller in the cross-plane direction, limited by weak van-der Waals interactions between layers. This suggests an alternative way to efficiently reduce the thermal conductance in nanostructures based on multilayer graphene. In this work, we investigate the thermoelectric properties of graphene junctions consisting of two monolayer graphene sheets coupled to each other along the cross-plane direction through a finite overlap, as schematized in Fig. 1. We propose to exploit this property to reduce the thermal conductance and finally to achieve high thermoelectric figure of merit  $ZT$  in graphene devices [9].

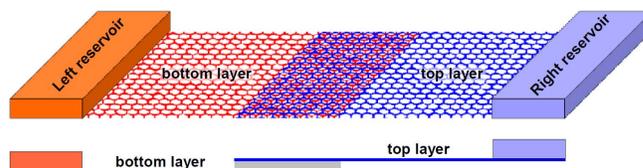


Fig. 1. Schematic view of vertical graphene device made of partially overlapped graphene layers.

## II. MODEL AND METHODOLOGY

Calculations were performed using an atomistic tight-binding Hamiltonian as in [10]. For the in-plane transport of phonons, a force constant model including four nearest neighbors [11] was used. To describe the coupling between graphene layers, we employed the spherically symmetric interatomic potential with the force constant matrix elements given by  $\Phi_{pq}^{ij} = -\alpha \exp(-\beta r) r_p r_q / r^2$ , with  $\alpha = 573.76 \text{ N/m}$  and  $\beta = 20 \text{ nm}^{-1}$  [12]. Since the length of studied devices (a few tens of nm) is smaller than the typical mean free path of electrons and phonons in graphene, both electrons and phonons were assumed to travel ballistically and independently. The ballistic electron and phonon transmission functions were hence calculated according to the nonequilibrium Green's function formalism [5]. From these transmission functions, the Landauer formalism was used to calculate the electrical conductance  $G_e$ , the Seebeck coefficient  $S$  and the thermal conductance  $K$  that determine the thermoelectric figure of merit

$ZT = TG_e S^2 / K$ . In the structures under study (Fig. 1), the key parameter is the junction length, i.e., the number of unit cells  $N_J$  in the overlap area of the graphene sheets (bilayer section).

### III. RESULTS AND DISCUSSION

#### A. 2D Graphene sheets

In Fig. 2, we display some basic transport quantities of vertical junctions made of two 2D graphene sheets ( $J121$ -junctions). As expected, the phonon transmission in this junction is strongly reduced (Fig. 2(a)), compared to the case of a single pristine graphene sheet, while the electrical transmission is not strongly affected (Fig. 2(b)). In Fig. 2(c, d), we plot the phonon conductance as a function of temperature and junction length  $N_J$ , respectively. We observe a significant reduction of phonon conductance in the  $J121$ -junctions when the junction length  $N_J$  is reduced. Though this ballistic phonon-conductance increases continuously when increasing the temperature, the increase rate becomes very weak in the high temperature regime (for  $T > 200$  K), compared to that in single-layer graphene (see also the data plotted in Figs. 3 and 4 discussed later). The former results from the enhancement of interlayer coupling between two graphene sheets when increasing their overlap area while the latter comes from the fact that the contribution of high-energy phonons in the  $J121$ -junctions is strongly suppressed (see Fig. 2(a)). Hence, it is expected that high  $ZT$  can be achieved when  $N_J$  is short enough in devices based on this kind of two-layer junctions, even at high temperature. For instance, as shown in Fig. 2(d), the ballistic phonon conductance at room temperature is reduced by  $\sim 92\%$  in the case of  $N_J = 5$  ( $\sim 2.2$  nm), compared to that in pristine graphene. It is in contrast with the behavior of the electronic transmission that is not strongly affected by the use of vertical junctions.

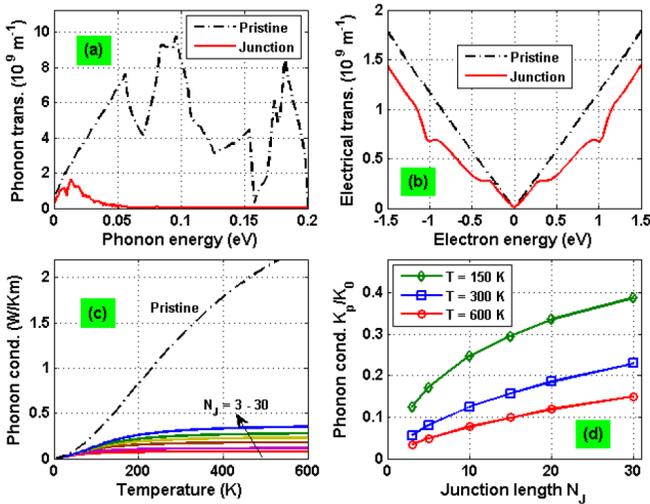


Fig. 2. Basic transport properties of devices made of two 2D graphene layers. The junction length  $N_J$  denotes the size of the overlap region between top and bottom layers.

#### B. Armchair graphene nanoribbons

However, the interesting properties observed above are not enough to achieve strong thermoelectric effect that usually requires materials with finite energy gap to provide a high Seebeck coefficient. We thus propose to replace the 2D graphene sheets in the junction by semiconducting armchair GNRs, i.e., to combine low thermal conductance and high Seebeck effect. In Fig. 3, we show the phonon conductance, the electrical conductance, the Seebeck coefficient and figure of merit  $ZT$  obtained in the  $J121$ -junctions made of 12-armchair GNRs, i.e. GNRs with 12 dimers along their width [13]. We would like to notice here that because of differences in electronic structure between monolayer and bilayer sections, confinement effects manifest themselves on the electron transport through the considered junctions, which results in the peaks and valleys of conductance. It may have important effects on other quantities, as shown especially for  $N_J = 12$ .

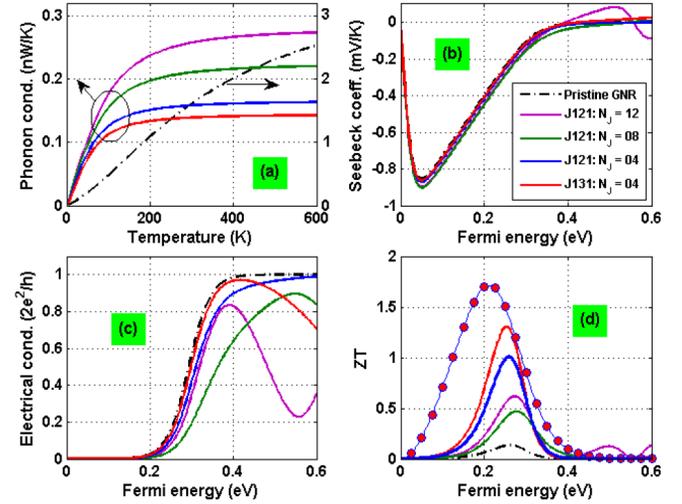


Fig. 3. Transport and thermoelectric properties in devices made of armchair nanoribbons. GNRs with 12 dimers along their width were considered here.  $J121/J131$  denote junctions without/with one more layer in the overlap region.

It is shown in Fig. 3 that these junctions provide (i) low phonon conductance (one order of magnitude smaller than that of a single layer GNR), and (ii) high Seebeck coefficient (up to  $\sim 0.9$  mV/K), without significant degradation of the electrical-conductance, compared to that obtained in the pristine GNR counterpart. As a consequence, values of  $ZT$  higher than 1 can be achieved at room temperature when the junction length is short enough (see the case of  $N_J = 4$  displayed in Fig. 3(d)), while the maximum value of  $ZT$  is just about 0.13 in the single pristine GNR. We observe once again that the phonon conductance increases and hence  $ZT$  is reduced when increasing  $N_J$ . Interestingly, because of the weak increase of ballistic phonon conductance at high temperature,  $ZT$  can more easily reach values higher than 1 when increasing the temperature, e.g., the maximum value of  $ZT$  is about 1.72 at 600 K while it is 1.02 at 300 K in the case shown in Fig. 3(d). A similar increase of  $ZT$  with the temperature is also observed in the pristine GNR (not shown) but to a much smaller extent (i.e., from 0.13 at 300 K to about 0.16 at 600 K) than in the vertical junctions. It is remarkable that such high  $ZT$  values can

be achieved at relatively low energy ( $< 0.3$  eV), i.e. at energy reachable in actual devices.

Our study also suggests that one can further suppress the phonon conductance by inserting a few additional graphene layers between the two graphene sheets of Fig. 1, leading, therefore, to a higher  $ZT$ . Indeed, as displayed in Fig. 3, the data obtained in a vertical junction with one additional GNR layer inserted in the overlap region ( $J131$ -junction) shows a reduced phonon conductance and an enhanced  $ZT$  ( $\sim 1.31$  at room temperature), compared to the case of  $J121$ -junctions ( $\sim 1.02$ ). However, we have also found out that inserting more graphene layers into the junction is not really an efficient way to further enhance  $ZT$ . Indeed, while the reduction of phonon conductance is weak, the electronic transmission of the junction can be significantly degraded by increasing the number of graphene layers. Hence, we should actually consider that the  $J121$ - and  $J131$ -junctions are the best compromise to get the balance between high electrical performance and low thermal conductance.

### C. Misoriented chiral graphene nanoribbons

To achieve high thermoelectric performance in GNR devices, our study shows that narrow armchair GNRs are required. Recently, it has been suggested that the use of misoriented layers that partially overlap each other could be a promising strategy to open a conduction energy gap in graphene devices [15]. However, though a finite gap is achieved in devices made of 2D misoriented layers, with a Seebeck coefficient significantly enhanced under strain effects, the power factor and hence  $ZT$  are still limited in this type of devices. To further increase the power factor, we propose to use devices made of misoriented GNRs.

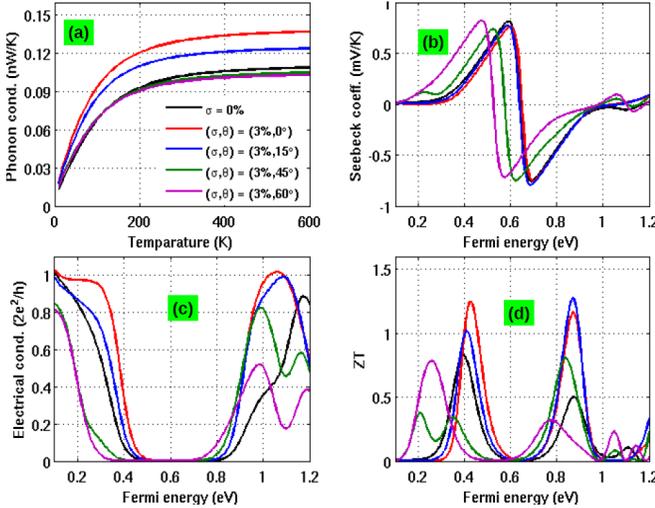


Fig. 4. Transport and thermoelectric properties in devices made of misoriented chiral GNRs. Here, the GNRs width is about 2 nm. The strain  $\sigma$  is applied (along the direction  $\theta$  with respect to the transport direction).

The idea is that (i) by combining the misorientation, edge chirality and confinement effects, a significant energy-gap of conductance can be achieved in devices made of relatively large GNRs while (ii) uniaxial strain can be used as an

additional ingredient to modulate the electronic transport [15] and hence to enhance the power factor. As an example, we have constructed a structure from two misoriented graphene layers with a twist angle of  $21.8^\circ$  and a small overlap. We then cut in this structure a stripe formed of two chiral GNRs with edges perpendicular to the overlap region. The transport properties in this device results from a complicated mixture of the different effects of misorientation, confinement, edge chirality and strain, but it is shown in Fig. 4 that a significant conduction gap of a few hundreds of meV and a  $ZT$  of 1.25 can be obtained at room temperature for a strain  $\sigma = 3\%$ . Further optimization of all these ingredients should certainly enhance this thermoelectric performance.

### D. Graphene nanomesh

To achieve high  $ZT$  in 2D graphene channels, we now suggest to use a graphene nanomesh (GNM) lattice as bottom graphene sheet. A GNM lattice consists in a graphene layer with a periodic array of nano-holes to open a finite energy gap [11], [14], [16], [17]. Among other possible applications, it has been predicted that it may enhance significantly the overall performance of graphene transistors [18]. Here, we have considered a square graphene nanomesh (GNM) lattice with periodic nanoholes obtained by removal of 26 carbon atoms in a super-cell of 140 atoms. Note that the use of GNM lattices in the top or in both graphene sheets can have the same effects.

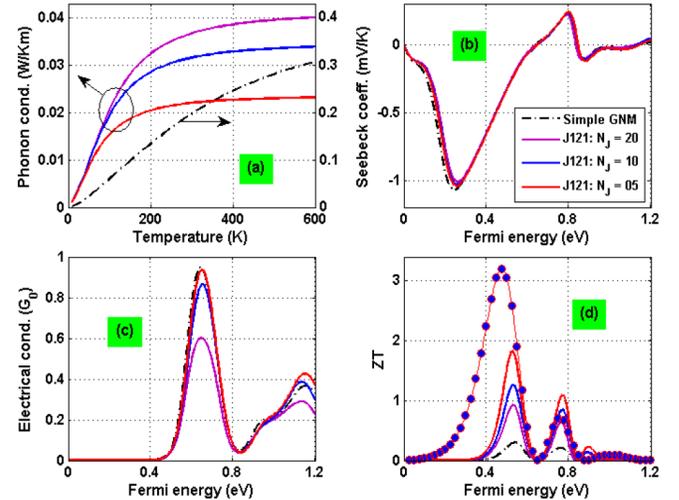


Fig. 5. Transport and thermoelectric properties in devices made of 2D graphene nanomesh lattices. Here, we considered square graphene nanomesh lattices with periodic nanoholes obtained by the removal of 26 carbon atoms in a super-cell of 140 atoms.

We show in Fig. 5 the phonon conductance, the electrical conductance, the Seebeck coefficient and the figure of merit  $ZT$  obtained in GNM-based  $J121$  junctions. The occurrence of conductance peaks and valleys is essentially due to mini-bands and mini-gaps in the bandstructure of GNM lattices [11]. In the case of a single GNM lattice, even if  $S$  is enhanced,  $ZT$  is still limited (to a maximum value of about 0.3 here) because the phonon conductance remains high. Obviously, the thermoelectric effect is greatly improved in the GNM-based  $J121$  junctions. Again, while the electrical performance ( $G_e$  and

$S$ ) is weakly affected (see Fig. 5(b,c)), the phonon conductance is strongly reduced, by a factor greater than ten at high temperature (see Fig. 5(a)), compared to the case of the single GNM lattice counterpart. Hence,  $ZT$  can reach the value of 1.8 at room temperature for  $N_f \leq 10$ . It can even get the very high value of 3.2 at the temperature of 600 K (see Fig. 5(d)).

#### IV. CONCLUSION

We have shown that using of junctions consisting of two partially overlapped graphene layers, high thermoelectric efficiency can be achieved in graphene devices. Thanks to the weak van-der Waals interactions between graphene layers, it is indeed possible to strongly reduce the phonon conductance while keeping the electronic conductance less affected. By making use of finite gap nanostructures (GNRs, GNMs) or finite conduction gap in misoriented graphene bilayers, high thermoelectric power can be achieved. This strategy finally results in values of thermoelectric figure of merit  $ZT$  higher than 1.5 at room temperature and higher than 3 at 600 K. It is also remarkable that in some cases, these high values of  $ZT$  can be obtained at relatively low Fermi energy. This type of multi-layer engineering is thus very promising to control independently charge and thermal transport in graphene devices and to achieve efficient thermoelectric energy conversion.

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