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Nanostructuration of Graphene Nanoribbons for thermoelectric applications

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Atomistic simulations of electron and phonon transport are performed within the non-equilibrium Green's function formalism to analyze the thermal and electrical properties of graphene nanoribbons (GNRs). We predict that by patterning GNRs properly, a strong enhancement of thermoelectric properties can be achieved. From the study of edge orientation effects, we propose a strategy likely to degrade the thermal conductance while retaining high electronic conductance and thermopower. An effect of resonant tunneling of electrons is evidenced in mixed GNRs consisting in alternate zigzag and armchair sections or in perfect GNRs with vacancies. Combining these effects, an optimized structure able to provide a high thermoelectric factor of merit *ZT* exceeding unity at room temperature is demonstrated.

I. INTRODUCTION

Recently, much attention has been focused on thermal [1] and thermoelectric [2] properties of graphene structures. For a two dimensional graphene sheet a "giant" Seebeck coefficient has been predicted [3] and the extremely high thermal conductivity of about $5kWm^{-1}K^{-1}$ has been measured [4]. Additionally, the phonon contribution to the thermal conductivity is expected to be strongly dependent on the GNR structure and significantly reduced by edge disorder at some specific phonon frequencies, which provides a possibility of designing devices with specific temperature-dependence of the thermal conductivity [5]. Such promising results have oriented many works on thermoelectric properties in GNRs [6]. Recently, it has been predicted that the thermoelectric figure of merit ZT can exceed unity in honeycomb chains of carbon atoms [7] and also in long rough edge GNRs [8]. However, detailed information on the potential of short GNRs to provide a high figure of merit ZT at room temperature in ordered structures is still missing.

In this article, we analyze the influence of the GNR lattice structure on the electron and phonon transport with a view to identify a strategy making possible to achieve good thermoelectric properties and in particular a high thermoelectric factor of merit *ZT* defined as $ZT = T G_e S^2 \kappa^{-1}$, where G_e is the electronic conductance, S is the thermopower (or Seebeck coefficient) and $\kappa = \kappa_e + \kappa_{ph}$ is the thermal conductance composed of electron and phonon contributions κ_e and κ_{ph}, respectively. As graphene has not intrinsically good thermoelectric performance due to its high thermal conductance, our strategy consists of designing specific structures where the phonon transmission and thus the thermal conductance are degraded while the electronic conductance and the thermopower are still high or even enhanced. We will show that it may be obtained by alternating GNR slices of different widths and edge orientations or by introducing periodical vacancies, which strongly reduces the thermal conductance and gives rise to an effect of resonant tunneling of electrons. Taking advantage of this phenomenon and from strongly reduced phonon thermal conductance, ZT values exceeding unity are then achieved at room temperature.

To fabricate these structures, the technological challenge of controlling precisely the ribbon edges at the atomic scale is expected to be overcome soon. Rapid progress in technology has been achieved in this direction [9-11].

II. MODEL AND METHODOLOGY

For the simulation of charge transport in graphene devices the most widely used approach is based on the powerful non-equilibrium Green's function (NEGF) formalism to treat either the continuous Dirac Hamiltonian in 2D graphene sheets [12,14] or an atomistic tight-binding Hamiltonian in GNRs [15-18]. Different semiclassical and quantum approaches have been developed for the phonon transport, such as molecular dynamics [19], transfer matrix [5] or even NEGF [20] and real-space Kubo [21] approaches. Recently, the investigation of the thermoelectric properties in GNR structures has been performed within the NEGF formalism to calculate both the electron and the phonon transmissions on an equal footing [6, 8]. In most of these works, a simple nearest-neighbor tight-binding (NNTB) Hamiltonian without edge relaxation was used for electrons, while a force constant model (FCM) including the fourth nearest-neighbors [8] was considered for phonons.

In this work, a phonon Hamiltonian based on a fifth nearest-neighbor FCM [22-23] and an NNTB electron Hamiltonian including armchair edges relaxation fitted from first principle calculation [24] were used. Ab initio simulations have demonstrated that the relaxation of armchair edges significantly changes the edge bond length and tight-binding parameters [25]. This effect has been predicted to be much smaller for zigzag edge bonds [26]. In our work the bond relaxation is included using two different

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TB parameters: the hopping energy of 3.02 eV is used for armchair edge bonds [25] and the standard value of 2.7 eV is used for internal and zigzag edge bonds as in relaxed 2D graphene. It is important to note that for AGNRs which are found to be metallic when using a single hopping parameter, a small band gap opens when considering the edge relaxation through a specific edge hopping parameter. In that follows, such AGNRs will be termed "quasi-metallic".

Due to the weak electron-phonon coupling in GNRs [27], in our approach both phonon and electron populations are assumed to travel ballistically and independently. The electron (phonon) transmission function $T_{e(ph)}$ is calculated according to the NEGF formalism. The Landauer formalism is applied to calculate phonon and electron fluxes. Finally, the thermopower S and the electronic contribution to the thermal conductance κ_e are calculated as detailed in Ref.[28]. The surface Green's functions and the device Green's functions are calculated using the fast iterative scheme proposed in [29] and the recursive algorithm described in [30], respectively.

The ribbons are defined by their edge orientations and the number n of dimmers in the unit cell which is related to the ribbon width W. Here three types of ribbon are considered: GNRs with armchair, zigzag and mixed edges are denoted by n-AGNR, n-ZGNR, and n-MGNR, respectively. The MGNR edges can be seen as a mixture of armchair and zigzag edges in the elementary cell, which, as the chirality of a carbon nanotube, may be fully characterized by a couple of numbers, giving the numbers of AGNR and ZGNR elementary cells, respectively, in the MGNR unit cell. All simulations are performed for devices consisting in a GNR active zone coupled with two semi-infinite contacts with the same structure.

III. Effect of Edge Orientations.

We study here the effect of GNR orientation on electron and phonon conductance. In Fig. 1 the thermal conductance κ_{ph} is plotted as a function of temperature for a 16-AGNR, 16-ZGNR and for a 16-MGNRs of "chirality" (5,1). In spite of their structural differences, perfect AGNR and ZGNR with the same number of dimmers in the elementary cell have a similar thermal conductance. Because of weak phonon transmission MGNRs exhibit lower thermal conductance than perfect AGNRs or ZGNRs, which results from the discrepancy between AGNR and ZGNR vibrational modes [23]. In particular, the specific phonon modes of AGNRs are suppressed in ZGNRs and vice versa. The thermal conductance at room temperature decreases from 2.5 nW/K for the perfect 16-AGNR to 1.4 nW/K for the 16-MGNR with "chirality" (5,1).

It is remarkable that the reduction on κ_{ph} in MGNRs is not accompanied by a drastic reduction of electronic conductance. ZGNRs are always gapless and AGNRs have an n-dependent bandgap width. For this reason in MGNRs armchair edges induce a band gap opening while zigzag edges generate gapless edge localized states, which has been verified experimentally [31]. Hence, the presence in the same elementary cell of both types of edges gives rise to very specific electron transport properties. Indeed, the ribbon sections with armchair edges can be seen as barriers between localized zigzag edge states and an MGNR can be seen as a multi barrier system. It induces a resonant tunneling transport regime which manifests through the strong oscillations of G_e observed in Fig. 2 which shows also a conduction bandgap of 300 meV in the MGNR (5,1).

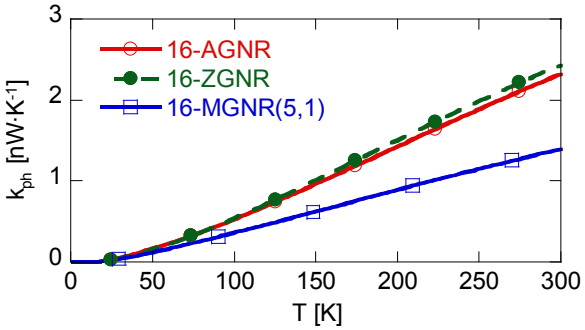

Figure 1: Phonon contribution κ_{ph} to thermal conductance as a function of the temperature T

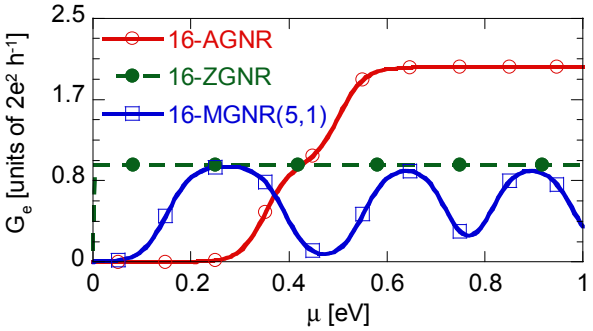

Figure 2: electronic conductance G_e as a function of the chemical potential μ

However, the resulting enhancement of S and ZT in MGNR is still limited compared to perfect 16-AGNR [32]. The maximum value of ZT is improved by about 50% and reaches 0.15, which is not enough for applications.

IV. Transport in Defected GNRs

Another strategy to degrade the high intrinsic thermal conductance of graphene consists in introducing lattice defects. In this work we consider simple atom vacancies. In Fig. 3 is plotted the thermal conductance as a function of the temperature for a perfect 13-AGNR and 13-AGNRs with one, two or three atom vacancies. The thermal conductance decreases when increasing the number of the vacancies.

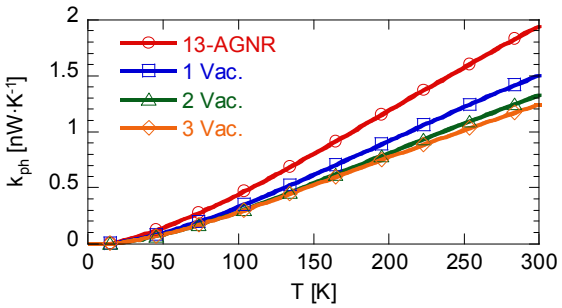

Figure 3: Phonon contribution κ_{ph} to thermal conductance as a function of the temperature T

Recent works have demonstrated that the strong reduction of thermal conduction due to random defects in the lattice is always accompanied by a degradation of electronic conductance, which prevents any ZT enhancement. This is not the case if defects are periodically generated in the center of the ribbon. In this situation a resonant transport,

similar to that observed in MGNR ones can appear and improve the thermoelectric properties.

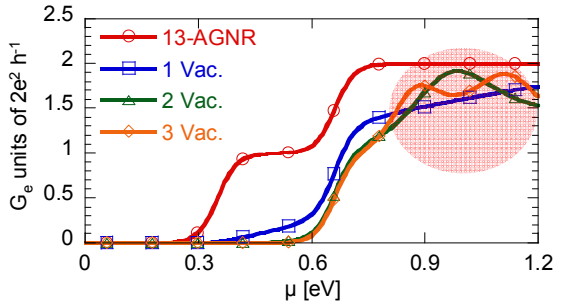

Figure 4: electronic conductance G_e as a function of the chemical potential μ

The resonance is illustrated in Fig. 4 where the electronic conductance is plotted for the same structures as in Fig. 3. Oscillations of electronic conductance appear at high energy for two or more vacancies. They are the signature of resonance between vacancy states. This is confirmed in the map of local electron density of states (LDOS) at the resonant energy (Fig. 5): electrons are fully localized around vacancies.

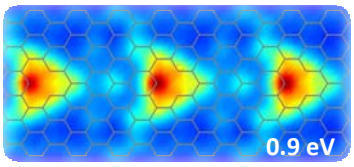

Figure 5: Atomic LDOS of the 13-AGNR with three vacancies calculated at 0.9 eV.

The only presence of vacancies is not enough to strongly enhance the thermopower and *ZT*. However, we will see in the next section that combining resonant phenomena due to vacancies and MGNR design allows us to strongly improve the thermoelectric properties.

V. Optimized Multi-Junction GNRs

Now, with a view to achieve a high ZT factor we propose to design some optimized GNR structures likely to strengthen the resonant tunneling effect and to further degrade the thermal conductance. The strategy should follow two main principles: first the structure must degrade the phonon transport, and second it must enhance *S* without degrading G_e. Since it is established that a high energy band gap is desirable to achieve high thermopower values, the 10-MGNR with "chirality" (3,3), shown in Fig. 6, appears as a good candidate. Consistently with Ref [33], the thermal conductance can be strongly degraded using two different widths in the elementary cell. A second solution called multi-junction GNR or "MJGNR" in Fig. 6, is thus proposed. Starting from the 10-MGNR with chirality (3,3) the width of the ZGNR sections is increased. Finally to exploit the vacancy effect the previous structure with periodical vacancies in the AGNR section is analyzed.

For the three structures, the electronic conductance, the Seebeck coefficient and the factor of merit ZT are plotted in Fig. 7(a), (b) and (c), respectively. In Fig. 8 is presented the thermal conductance.

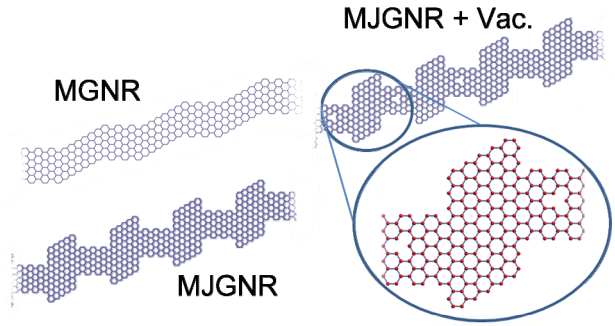

Figure 6: MGNR (3,3) alternating armchair and zigzag elementary cells with the same width, with different widths (MJGNR) and with different widths with vacancies (MJGNR+Vac.)

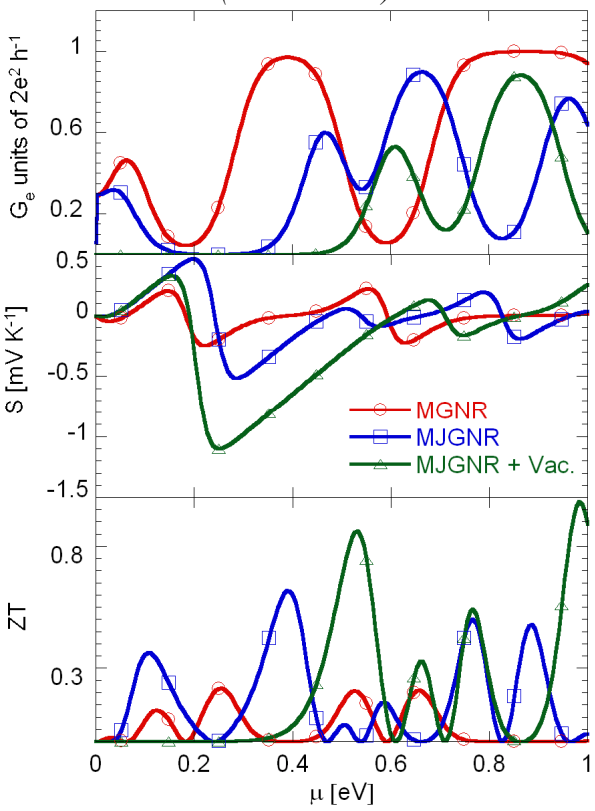

Figure 7: (a) Electronic conductance G_e, (b) Seebeck coefficient and (c) factor of merit ZT as a function of chemical potential μ

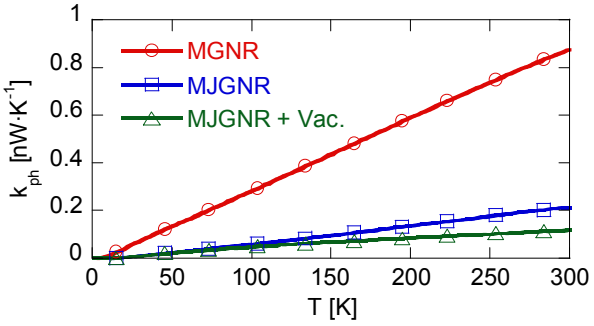

Figure 8: Phonon contribution to thermal conductance as a function of the temperature T.

Even if the thermoelectric properties of the MGNR are improved, compared with perfect GNRs, thanks to the electronic resonance and to the thermal conductance

reduction (see section III), this is not enough to achieve high *ZT* values. To enhance these two phenomena the MJGNR structure is proposed. For such structure the localized states associated with zigzag edges strengthen the resonant effects. They induce a strongly selective electronic transmission which manifests through strong oscillations in the electronic conductance (Fig. 7(a)). In this mixed structure, we observe the building of energy gaps and minibands which are not present in perfect AGNRs and ZGNRs. As a consequence of the strong resonant tunneling effect the thermopower S is significantly enhanced with respect to simple MGNR and exhibits strong oscillations from about -0.5 mV/K to 0.5 mV/K (Fig. 7(b)).

In parallel, the thermal conductance reduces drastically due to strong differences in phonon vibrational modes between the different sections of the ribbon and it reaches a very low value smaller than 0.2 nW/K at room temperature (Fig. 8). It is worth noting that while the electron thermal conductance was negligible in AGNRs, ZGNRs and even in MGNRs, it is now comparable to the phonon thermal conductance (not shown), which is a consequence of the strong reduction of the latter. It is thus important to include the electron contribution to the thermal conductance in the calculation.The combined effect of the thermopower enhancement and of the reduced thermal conductance finally boosts *ZT* which exceeds 0.6 at room temperature as shown in Fig. 7(c).

Such results can be further improved by adding vacancies in the previous structure. The major effect is the broadening of the electron energy band gap, which shifts the resonant curve of electronic conductance of MJGNR structure at higher energy (Fig. 7(a)). A direct consequence is the strong enhancement of thermopower. If we combine this result to the reduction of thermal conductance visible in Fig. 8, *ZT* values can exceed unity value. It is a remarkable result for possible thermoelectric applications of graphene nanoribbons.

VI. CONCLUSION

In summary, a specific patterning of a mixed GNR obtained by alternating armchair and zigzag sections of different width and with periodical atom vacancies has been shown to provide high thermoelectric performance with a ZT factor reaching unity at room temperature. It results from the combination of (i) very small phonon thermal conductance due to the mismatch of phonon modes in the different sections and (ii) the resonant tunneling of electrons between these sections which retains high electron conductance and thermopower.

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