Ab Initio Study of Phonon-Induced Dephasing of Electronic Excitations in Narrow Graphene Nanoribbons

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Introduction

Perhaps the greatest driving force for the study of graphene is its potential to replace the channel material in field effect transistors (FET) [1]. Single-walled carbon nanotubes (SWCNT) were once expected to hold this honor, however the mixture of semiconducting and metallic SWCNTs produced during synthesis is a major roadblock. Although large graphene sheets are zero band-gap semi-metals, it has been shown theoretically [2, 3] and experimentally [4, 5] that quantum confinement effects in narrow graphene nanoribbons (GNR) cause an opening of the band gap. This important verification allows for the patterning of GNRs in FETs without the difficulties associated with SWCNTs. Further, it was recently demonstrated that GNR FETs may be etched lithographically to a size of less than 10 nm [4]. This is an important landmark, since current Si-based FETs are built using lithographic techniques. As GNRs are envisioned as an electronic material of the future, a detailed knowledge of their fundamental properties is of the utmost importance.

The electron-phonon interaction influences the electron mean-free-path in nanoribbon FETs and, therefore, determines the length of the FET channel as well as the switching speed of the device [1]. The electron-phonon interaction and phonon-induced electronic dephasing can be expected to play important roles in many other potential applications of GNRs. Charge-phonon scattering will be the main source of energy dissipation and loss in future GNRs electronic devices. Phonon induced electronic dephasing sets coherence limits on spin [6] and charge transport [7]. Electron-phonon interactions can create distortions in GNR geometry structure and, therefore, affect many of their mechanical and electronic properties.

Methods

The current simulation uses the (16,16) armchair GNR with a width of 1.8 nm. The dangling bonds on the edges of the GNR are terminated with hydrogens. The Stone-Wales (SW) and 7557 defects chosen here are well known for SWCNTs [8] and represent the same disruption in the perfect hexagonal periodicity of graphene, obtained by different means. The SW defect is a rotation of a C-C dimer in the plane of the GNR. The 7557 defect involves insertion of a C-C dimer and leads to a much larger distortion in both the electronic and geometric structure. While the GNR with the SW defect remained relatively flat during the simulation, the 7557 caused a large buckling of the ribbon (Fig. 1d). The SW and 7557 changes in the bonding pattern are relatively minor, since they do not involve dangling bonds or heteroatoms, though they have been shown to affect the reactivity of SWCNTs [9]. Generally, one can expect that changes in the GNR properties will be similar but more pronounced with more major defects.

The molecular dynamics (MD) simulations were performed using the Vienna Ab Initio Simulations Package [10]. The Perdew-Wang generalized gradient approximation [11] with projector-augmented-wave pseudopotentials [12] was employed in a converged plane-wave basis. Periodic boundary conditions were used along the length of the GNRs and five unit cells were incorporated in order to expand the phonon spectrum. 8 Å of vacuum were used in the directions perpendicular to the length of the ribbon in order to avoid spurious interactions. All ribbons were relaxed to their minimum-energy geometries and then heated to 300K via repeated velocity rescaling. Trajectories were obtained using the Verlet integration algorithm and Hellmann-Feynman forces in the microcanonical ensemble. Distortion of the 2D lattice due to the 7557 defect was not observed during the energy minimization and only occurred during the MD run, indicating that defect relaxation involves an energy barrier. The data involving the defect relaxation was removed from the analysis.

The dephasing function can be obtained based on the evolution of the corresponding electronic energy gap ΔE

$$D(t) = \exp\left[i\langle \Delta E\rangle_T t/\hbar\right]\left\langle \exp\left\{-\frac{i}{\hbar}\int_0^t \Delta E(\tau)\,d\tau\right\}\right\rangle_T . \quad (1)$$

An estimate of the dephasing time may be also calculated using the second order cumulant expansion, which gives a perturbative description of the optical response function [13].

Results and Discussion

The dephasing functions for the ideal GNR and the GNRs with the defects are qualitatively different and were fit with two separate equations in order to extract the dephasing timescales. The dephasing function of the ideal ribbon was fit using

$$f_A(t) = \exp\left(-t/\tau\right)\frac{1+A\cos(\omega t)}{1+A}, \quad (2)$$

where ω is the frequency of the oscillations seen on top of the decay. The GNRs with defects showed little oscillations, but required a Gaussian component in order to obtain a good fit:

$$f_B(t) = \left[B\exp\left(-t/\tau_e\right) + (1-B)\exp\left(-t/\tau_g\right)^2\right]. \quad (3)$$

Here, B gives the magnitude of the exponential decay component. The fitting results are shown in Table 1. The frequency ω obtained from the ACF fit (2) corresponds to the 1345cm^{-1} phonon mode.. The absorption and emission linewidths, Γ, presented in the table are calculated using the formula

$$\Gamma = \frac{\hbar}{T_2^*} \quad (4)$$

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TABLE I: Pure-dephasing times T_2^* and corresponding homogeneous linewidths Γ, obtained by fitting the cumulant and direct dephasing functions to Eqs. (2) and (3), respectively. The first/second number in each cell corresponds to the cumulant/direct calculation.

Ribbon	τ (fs)	ω (fs^{-1})	A	Γ (meV)
(16,16)	23.5/25.8	0.259/0.257	0.024/0.069	28.0/25.5
Defect	τ_e (fs)	τ_g (fs)	B	Γ (meV)
7557	41.8/48.9	39.9/35.7	0.38/0.30	16.1/16.5
SW	69.8/57.3	42.3/46.0	0.54/0.44	11.5/12.9

where the pure-dephasing time $T_2^* = \tau_e$ is taken from the fit (2) for the ideal GNR and $T_2^* = [B\tau_e + (1-B)\tau_g]/2$ is taken from the fit (3) for the GNRs with defects.

Both direct and cumulant schemes show that the defects slow down the dephasing process in GNRs. This surprising discovery is in stark contrast with SWCNTs, in which the 7557 and SW defects accelerate the dephasing [14]. As with SWCNTs, the defects induce a large amount of disorder into the phonon spectrum and allow for coupling to a larger range of modes. However, the electron-phonon coupling is weaker with defects compared to the ideal ribbon. The average fluctuation of the excitation energy cased by the vibrational motions is larger in the ideal ribbon by a factor of four. This difference in the fluctuation amplitude has a more profound effect on the dephasing function than the faster decay of the ACFs seen with the defects. Comparing the two defects between each other, we observe that the electron-phonon coupling is weaker with the SW defect and the dephasing is slower in this case. This corresponds very well to SWCNTs [14], in which the stronger 7557 defect induces faster dephasing as well. In fact, the pure-dephasing times calculated for the SW defect in the GNR and SWCNT [14] are very similar. The pure-dephasing times calculated for the 7557 defect are different between the GNR and SWCNT. Due to its intrinsic flexibility, the GNR is able to accommodate the defect and relax its geometric strain much more easily than the SWCNT. As a result, the dephasing induced by the 7557 defect is slower in the GNR than in the SWCNT.

The linewidths calculated on the basis of the dephasing times using Eq. (4) can be used experimentally to establish the presence of defects. The calculation predicts that the optical lines should be broader in the ideal GNRs than in the GNR with the defects. The difference in the linewidth is about a factor of two for the current GNRs. The situation is reversed from the SWCNT case, in which defect can be detected by broader, rather than by narrower optical bands [14, 15]. The optical bands of ideal GNRs are broader than the bands of the ideal SWCNTs, because GNRs are less rigid than SWCNTs and allow for stronger electron-phonon coupling.

Conclusions

In conclusion, for the first time, we have applied *ab initio* molecular dynamics in order to investigate the phonon-induced dephasing and linewidths of the lowest energy electronic excitations in a narrow GNR with and without defects. The method was tested previously with similar size SWCNTs [14] as well as quantum dots [16], and gave excellent agreement with the experimental data. Compared to the perfect nanotubes, the dephasing in the perfect nanoribbon is a factor of two faster, because the nanoribbon is less stiff than the nanotubes and exhibits larger scale energy fluctuation. The homogeneous optical linewidth associated with the pure-dephasing process is twice larger in the GNR than in SWCNTs. The dephasing in the ideal ribbon is induced primarily by the disorder mode seen in bulk graphite. In contrast to the nanotubes, defects in the nanoribbon slow down the dephasing. The dephasing induced by the bond-rotation defect is very similar in both GNR and SWCNT. The bond-insertion defect behaves differently in the two materials, because the nanoribbon can relax the strain induced by the defect, while the defect remains strained in the nanotube. The fact that the electron-phonon interaction induced by the defects is weaker than the interaction in the ideal GNR has very important practical implications. In particular, it ensures that the problem of defect-induced fluorescence quenching and energy dissipation, which limits many applications of semiconducting SWCNTs, should not arise with GNRs.

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