



Effect of boron and nitrogen doping with native point defects on the vibrational properties of graphene



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ARTICLE INFO

Article history:

Received 5 November 2013

Received in revised form 8 January 2014

Accepted 21 January 2014

Available online 15 February 2014

Keywords:

B- and N-doped graphene

Vibrational properties

Phonon localization

ABSTRACT

Boron and nitrogen doping in graphene has important implications in graphene-based devices. We investigate systematically the vibrational properties of B- and N-doped graphene with vacancies using forced vibrational method. We have calculated the phonon density of states (PDOSs), typical mode patterns and phonon localization length for different concentration of B, N and vacancies. We find that the interference between native point defects and B or N dopant break down the phonon degeneracy at the Γ point of the LO and TO modes, distort and shift down the PDOSs significantly. We observe a broadening and softening of the Raman active E_{2g} phonon mode with an increase of B and N atoms. The PDOS peaks for the mixture of vacancies and B or N atoms show the remarkable increase in the low-frequency region induced by their defect formations. Our computer experiments demonstrate that the disordered graphene show the spatially localized vibrations due to the resonant vibrations of the impurity atoms relative to the main C atoms. The calculated typical mode patterns for in-plane K point optical phonon modes indicate that the phonon is localized strongly within a region of several nanometers in the random disordered graphene structures. In particular, a typical localization length is on the order of ≈ 9.5 nm for B- and N-doping, ≈ 9 nm for mixture of B-doping and vacancy, and ≈ 8.5 nm for mixture of N-doping and vacancy concentrations of 20%. This study provides a useful basis for the understanding of a wide variety of physical properties such as thermal conductivity, specific heat capacity, and electron–phonon interaction, as well as in the experiments of infrared, Raman, and neutron-diffraction spectra of doped-graphene.

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1. Introduction

Due to its excellent and novel properties [1–3], graphene has emerged as one of the most promising materials for the next generation electronics by overcoming silicon-based electronics limitations [4]. However, the electronic applications are handicapped by the absence of a bandgap in the pristine graphene [5,6]. The development of graphene based electronics depends on our ability to open a tunable bandgap. In the quest to opening and tuning an energy gap in graphene, various approaches have been developed to improve the semiconducting properties. To exemplify, metal to semiconductor transition is introduced by forming confined geometries of quantum dots [1], nanoribbons [7,8], nanomesh [9], or binding graphene to particular substrates [10,11]. The substitutional doping is one of the most feasible methods which can tailor the electronic band structure of graphene, and open up an energy gap between the valence band and the conduction band. Atoms such as B and N are the ideal candidates as dopants in graphene

because of their similar atomic size as that of C and of their hole acceptor and electron donor characters for substitutional B- and N-doping, respectively. B- or N-doped graphene-based materials have shown enhanced electrical properties relative to the materials without doping [12–14]. The semiconducting B- and N-doped graphene have also been successfully synthesized by chemical vapor deposition (CVD) and electrothermal reactions [15–17]. The tunable energy gap opening and doping dependent electronic properties of graphene make the vast application of graphene-based devices even more promising.

In addition to ideal systems, when graphene has been fabricated experimentally, they will have some structural defects. Vacancy and adatom-vacancy defects are among the most probable ones [18]. Vacancies have a striking effect on the electronic structure. In particular, it is well known that vacancies induce localized states with associated resonant peaks at the Dirac point, and that state in the vicinity of the Dirac point has an enhanced tendency for localization, as revealed by an enhancement of the electronic inverse participation ratio [19]. Recent experimental studies [20–24] imply that some mutual effects between structural defects and dopant atoms are present during the incorporation of heteroatoms into

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graphene. Hou et al. [25] analyzed the energetic stability of substitutional N dopants in graphene with vacancies and Stone–Wales (SW) defect. They demonstrated [26] from the total energy calculations based on density functional theory (DFT) that the native point defect and N dopant attract each other, i.e., they display cooperative effect, suggesting that N dopants can prompt the creation of point defects and vice versa. The formation of complexes between native point defect and N dopant strongly modifies the role of N doping regarding the free carrier production in the bulk π bands.

Electrons and phonons are strongly coupled in graphene-like sp^2 carbon systems [27] ensuing Kohn anomalies [28,29] and possible soft modes [30,31]. Because of free carrier-induced many body interactions, one expects the observed phonon energy in a doped system to be different from the bare phonon energy in an undoped system. It has been shown recently that the phonons in graphene are altered interestingly by tuning the applied gate voltage [27,32] and that the Raman spectroscopy has been used to measure the nature and level of doping-induced carriers. Mechanisms of molecular doping and the related chemical sensor properties of graphene have also been investigated [32,33]. Electronic band structure and phonon properties of aromatic molecules such as aniline and nitrobenzene using first principles calculations have been reported very recently [34]. It has been found recently that the electron or hole doping shifts the Raman frequency of the G band along with the decrease in its line width in the case of single walled carbon nanotube (SWCNT) [35] and graphene [36]. This shift in frequency is associated with the shifts in Fermi level and charge transfer between graphene and dopant atoms. Moreover, even small concentrations of vacancies in graphene-based structures may alter the phonon properties significantly and thus change their optical absorption, low temperature specific heat and transport properties. A detailed understanding of the vibrational properties of doped-graphene with native vacancy defects is thus of fundamental importance as they govern electron transport, and hence the performance of graphene-based electronic devices.

A large number of studies have been devoted to estimating the phonon properties of graphene over the past few years using various theoretical approaches including force constant fittings [37,38], density functional theory [29,30,39], and the first-principles calculations [40–42]. In contrast to the intensive research performed on the phonon properties of pristine graphene, the phonon properties of defective graphene have not been well studied. When impurities present in a system, they may induce the symmetry breakdown of elemental topological arrangements, which generate more complex lattice structures. Therefore, the dynamical matrix technique requires huge computational resources. These long computational times and convergence problems in the dynamical matrix calculations limit the systems of interest to benchmark molecules. However, a significantly larger scale model is essential for an in-depth understanding of vibrational properties of defective atomic structures. It is thus crucial to develop a reliable model to observe the vibration modes of disordered graphene-related materials directly.

Here we concentrate on the effects of B- and N-doping combined with vacancies on the phonon properties of graphene. Due to the presence of impurities in a crystal, there may appear vibrational modes [43,44] lying outside of the allowed frequency range of the perfect crystal. These are called localized vibrational modes or local modes because the mode energy is spatially concentrated near the defect site, which is similar to Anderson's localization for electronic wave functions in the disordered lattice. In general crystal imperfections give rise to localized excitations which can also limit the phonon life time through elastic or inelastic scattering. If the vibration modes or the phonons are localized, the mean free

path of the phonon becomes finite and proportional to the square of the localization length. When the interaction of electron and phonon of graphene has been discussed [45,46], the phonon wave function has been treated as delocalized in the crystal. However, owing to the presence of B and N atoms or vacancies in the graphene sample, phonons have a finite lifetime and a finite localization length due to the scattering by impurity atoms, which can contribute considerably to the natural line width of the Raman spectra. Hence, we require an insightful understanding on how the doping with vacancies way the lattice vibrations of graphene.

In this work, we present a more extensive and systematic numerical study of the vibrational properties of B- and N-doped graphene with native vacancies using the forced vibrational method useful for large and complex systems. We have computed the change of the phonon density of states for different concentration of B and N impurities or vacancies. We investigate the localization properties of phonon eigenstates and calculate the typical mode patterns due to the presence of B or N impurities and vacancies. We focus particularly on the K point in-plane transverse optical (iTO) mode phonons because of their importance in the Raman D band, the dominant feature in the Raman spectra. Moreover, we also calculate the localization length as a function of impurity density to study the localization effects caused by different types of impurities.

2. Theoretical details

2.1. Forced vibrational (FV) method

The forced vibrational (FV) method employed in the present work, introduced by Williams and Maris [47], enables us to treat the eigenvalue problem of very large systems. The fundamental idea is based on the physical analogy that the eigenfrequency of the system satisfies the resonance condition when applying the periodic external force with certain frequency to the system. In general, the equation of motion of the systems consisting of N atoms which are coupled together with linear springs, with the scalar displacement of the l th mass, $u_l(t)$ is:

$$M_l \ddot{u}_l(t) + \sum_r \varphi_{lr} u_r(t) = 0 \quad (1)$$

where M_l is the mass of the atom at site l , and φ_{lr} is the strength of the spring between atoms l and l' . The initial set at $t = 0$ is prepared in which all atoms are at rest and have zero displacements. A random force is applied to each atom at rest, which is given by:

$$F_l = F_0 \sqrt{M_l} \cos(\varphi_l) \cos(\Omega t) \quad (2)$$

where F_0 is a constant amplitude, the phase φ_l and Ω are a random variable with respect to the site number l and a frequency of the external force, respectively. The averaged total energy of the system after time T becomes:

$$\langle E(\Omega, T) \rangle = \frac{F_0^2}{4} \sum_{\lambda} \frac{\sin^2[(\omega_{\lambda} - \Omega)T/2]}{(\omega_{\lambda} - \Omega)^2} \quad (3)$$

where ω_{λ} is an eigenfrequency of mode λ . If one chooses the time interval T so that: (i) the resonance width $\Delta\Omega$ is small enough compared with Ω ; (ii) the number of modes in $\Delta\Omega$ is much larger than unity, one can approximate the summand in Eq. (3) by the δ function. As a result, one has the DOS of the system as:

$$g(\Omega) = \frac{8\langle E(\Omega, T) \rangle}{\pi F_0^2 N} \quad (4)$$

In order to obtain the DOS, our task is to compute the averaged total energy $\langle E(\Omega, T) \rangle$.

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