Phononic band gap engineering in graphene

A. Sgouros,¹ M. M. Sigalas,¹ G. Kalosakas,¹,² K. Papagelis,¹,² and N. I. Papanicolaou³
¹Department of Materials Science, University of Patras, 26504 Patras, Greece
²Institute of Chemical Engineering Sciences - Foundation of Research and Technology Hellas (FORTH / ICE-HT), 26504 Patras, Greece
³Department of Physics, University of Ioannina, P. O. Box 1186, GR-45110 Ioannina, Greece

(Received 13 June 2012; accepted 3 October 2012; published online 2 November 2012)

Using ab initio and molecular dynamics simulations with semi-empirical potentials, the phonon density of states (PnDOS) of graphene with different types of defects such as substitution atoms (Si), carbon isotopes (¹²C and ¹⁴C), and vacancies was calculated. The main interest was to investigate the possibility to generate phononic band gaps (PBGs) in the PnDOS of graphene, since the derived structures may have sufficiently low thermal conductivity and find applications in improved thermoelectric materials. From all the studied defect types, the silicon substitution is the only one that creates PBGs. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4763479]

INTRODUCTION

Phononic crystals (PnCs) have attracted a lot of interest over the last two decades due to their possible applications in sensors and radio frequency (RF) filters and the ability to control acoustic and elastic waves. They are artificial composite materials made of periodic distribution of inclusions embedded in a matrix. Due to their periodic structure, these materials may exhibit under certain conditions, phononic band gaps (PBGs)—a frequency region where no acoustic or elastic wave propagation is allowed.

More recently, there is an intense effort in nanoscale PnCs to control phonon propagation in these materials. Experiments in silicon slabs with phononic crystals formed by periodically placing holes have measured thermal conductivities significantly lower than in bulk silicon. Besides, early theoretical studies showed reduction of thermal conductivity in one dimensional phononic crystals due to the strong modification of the phonon group velocities. Further, theoretical calculations provided evidences that superlattices can affect the phonon propagation, and thus, reduce the thermal conductivity. Recent studies with semiempirical potentials and molecular dynamics (MD) simulations in silicon with nanometer size phononic crystals have also showed the interplay between phonon dispersion and reduced thermal conductivity. Similar calculations on nanoporous silicon showed that the figure of merit (which is proportional to the ratio between the electrical conductivity and the thermal conductivity) increased by two orders of magnitude relative to the bulk silicon mainly due to the significant attenuation of the thermal conductivity. In this context, nanometer scale phononic crystals made of germanium quantum dots periodically placed in a silicon matrix, exhibit a significant reduction of the thermal conductivity by several orders of magnitude relative to the bulk silicon. Consequently, the theoretical findings revealed that nano-phononic semiconductor crystals comprise promising structures to pursue novel high-performance thermoelectric materials.

In an attempt to overcome the efficiency barriers imposed by the physics of conventional bulk materials, low-dimensional systems offer promising “scaffolds” for designing thermoelectric materials, as novel electronic band structures arise and phonon engineering can be utilized. In addition to its remarkable properties, graphene exhibits extremely high thermal conductivity. Due to its two-dimensional crystal structure, the physics of phonons (the main heat conduction carriers) in graphene is unique. Very recent experimental and theoretical studies have shown a reduction of the thermal conductivity of graphene samples synthesized by the chemical vapour deposition method and having different isotope compositions. Also, MD simulations in graphene with phononic crystals made with periodic arrays of holes showed dramatic changes in phonon lifetimes due to the Bragg scattering. From all these studies, it is quite clear that affecting the phonon dispersion of the materials by creating PBGs will have an impact on the thermal conductivity of those materials.

In this work, the effect of various types of defects on the phonon density of states of graphene is theoretically investigated using both ab initio and empirical methods. Defects were introduced in graphene by (a) replacing carbon atoms with silicon, (b) replacing carbon atoms with other carbon isotopes, (c) removing carbon atoms, and (d) adding carbon atoms. We focus mainly in the capability to create phononic band gaps.

COMPUTATIONAL METHODS

The ab initio calculations are performed in the framework of the generalized gradient approximation (GGA) employing the exchange–correlation functional of Perdew, Berke, and Ernzerhof (PBE), expanding the wavefunction on plane-wave basis sets. The standard Vanderbilt ultrasoft pseudopotentials have been used. The plane-wave basis set cut-off is set to 280 eV. For the sampling of the Brillouin zone, a 6 × 6 × 1 Monkhorst–Pack mesh is used. Tight convergence criteria have been imposed for the total (self-consistent) energy per atom at 10⁻⁷ eV/atom. The threshold on the forces is set to 10⁻³ eV/Å. For the phonon density of states (PnDOS) calculations, the dynamical matrix is calculated on
a $6 \times 6 \times 1$ $q$-point mesh. All calculations are spin-unrestricted. A supercell is used in the direction perpendicular to the graphene layer with 2.5 nm size. The calculations have been performed using the electronic structure calculation package QUANTUM ESPRESSO.\textsuperscript{23} The molecular dynamics simulations are performed with an open source code\textsuperscript{24} using the Tersoff’s potentials for C–C, Si–Si, and C–Si interactions.\textsuperscript{25} A box containing a graphene layer with 1248 atoms has been used. In the direction perpendicular to the graphene layer, there is a 60 nm thick layer of empty space. Three different boundary conditions have been used at the edges of the box: free, fixed, and periodic. Since the PnDOS results are very similar for all these cases, the free boundary conditions are used in this study. The MD calculations correspond to a temperature 300 K, unless it is otherwise mentioned. The time step used in MD simulations is 0.9 fs. The phonon density of states of graphene at finite temperature has been calculated by Fourier transforming the velocity time autocorrelation function\textsuperscript{26,27}

\[ D(\omega) \propto \int_0^\infty e^{i\omega t} \sum I \left(V_I(t_0) \cdot V_I(t_0 + t)\right) dt, \]  

where $V_I$ is the velocity of atom I and the average $\langle ... \rangle$ is over the initial time $t_0$. After placing the atoms in their initial static equilibrium positions, an MD simulation with 50 000 time steps is performed so the atoms are relaxed in thermal equilibrium. Then, another 2000 time steps of the MD simulations are performed where the velocities of each atom are stored. These velocities are used for the calculation of the PnDOS from Eq. (1). We have tested that longer relaxation times, or longer simulation times for collecting data, do not modify the obtained results.

RESULTS AND DISCUSSION
In a previous study,\textsuperscript{28} using similar \textit{ab initio} calculations, it has been found that the PnDOS of graphene is characterized by fundamental modes up to 1660 cm$^{-1}$. Two local minima at around 995 cm$^{-1}$ and 1205 cm$^{-1}$ separated by a local maximum at 1105 cm$^{-1}$ can be clearly seen. These values are in good agreement with other \textit{ab initio} calculations.\textsuperscript{29} Here, similar PnDOS calculations are performed for a graphene layer having half of the $^{12}$C atoms periodically replaced by the isotope $^{14}$C atoms. The unit cell used in the calculation is shown in Fig. 1 (inset), where each $^{12}$C ($^{14}$C) atom has three $^{14}$C ($^{12}$C) atoms as nearest neighbors. The PnDOS for that structure has a similar shape to the pure graphene PnDOS, except for an almost uniform shift of about 4% towards the lower frequencies. The highest frequency phonon is at 1610 cm$^{-1}$, the two local minima are at around 955 cm$^{-1}$ and 1150 cm$^{-1}$ separated by a local maximum at 1055 cm$^{-1}$ (see Fig. 1). Direct comparison with the in-plane phonon dispersion of graphite,\textsuperscript{30} determined by inelastic x-ray scattering, gives further insight on the vibrational characteristics of graphene. More specifically, the phonon modes located in the high energy region 1200–1600 cm$^{-1}$ mainly originated from the in-plane transverse (TO) and longitudinal optical (LO) branches. The highest frequency part of the in-plane longitudinal acoustic (LA) branch dominates the vibrational spectrum in the range 950–1200 cm$^{-1}$. The observed low intensity of the one-phonon density-of-states reflects the significant dispersion of the aforementioned branch.\textsuperscript{30} The peak at 750 cm$^{-1}$ exhibits significant contribution from the out-of-plane optical modes (ZO) while the 600 cm$^{-1}$ one comes from the in-plane transverse acoustic (TA) and the ZO modes.

For isotopically pure graphene, the PnDOS calculated by MD simulations is shown in Fig. 2 with continuous line. The highest phonon frequency is at 1520 cm$^{-1}$. As in the \textit{ab initio} case, it has two local minima at around 960 cm$^{-1}$ and 1140 cm$^{-1}$, separated by a local maximum at 1040 cm$^{-1}$ (solid line in Fig. 2). In general, the features of the PnDOS obtained through MD calculations are shifted to lower frequencies by 6%–10% relative to the corresponding values from the first principles PnDOS. About 1% of that difference is due to the ambient temperature used in the MD simulation (compared to the zero temperature \textit{ab initio} calculations). For example, the highest frequency phonon appears at about 1540 cm$^{-1}$ for 50 K. Similar trends are observed when half of the $^{12}$C atoms are replaced in a periodic manner by $^{14}$C. In

\[ \text{FIG. 1. Phonon density of states (PnDOS) obtained from \textit{ab initio} calculations for the isotope distribution shown in the inset. Inset: The distribution of}$^{12}$C (gray) and $^{14}$C (yellow) carbon atoms in the isotopically defected graphene used in our \textit{ab initio} calculations. \]

\[ \text{FIG. 2. PnDOS obtained from molecular dynamics simulations for graphene (solid line). Dash line corresponds to periodically replacing half of the carbon atoms with atomic mass 12 to carbons with atomic mass 14 (as in the inset of Fig. 1). Dotted-dash line corresponds to the case where half of those}$^{14}$C and $^{12}$C atoms, randomly selected, are mutually interchanged with the other carbon isotope (see text).} \]
that case, the highest frequency phonon is at 1460 cm$^{-1}$, the
two local minima are at around 920 cm$^{-1}$ and 1110 cm$^{-1}$
separated by a local maximum at 1020 cm$^{-1}$ (dash line in
Fig. 2). So, there is a red shift of the features in the PnDOS
by about 3% relative to the similar features in isotopically pure $^{12}$C graphene. It should be noted that the aforementioned shift is almost similar to that encountered by the ab initio calculations in the previous paragraph. Further, the PnDOS does not change significantly by considering a random configuration of $^{13}$C and $^{14}$C atoms, keeping the overall percentage of each isotope at 50%. For example, starting from the ordered isotope configuration shown in the inset of Fig. 1 and mutually interchanging half of the $^{12}$C atoms with half of the $^{14}$C atoms in a random fashion, the PnDOS shown by dotted-dash line in Fig. 2 is obtained. Dotted-dash line in Fig. 2 shows the result for a single random realization, but similar curves are obtained for different realizations. Disorder does not seem to influence considerably the PnDOS characteristics in this particular case.

There were recent MD calculations of the thermal conductivity of graphene with artificially made holes. Similar structures were examined here in order to find whether they exhibit any phononic band gaps. Figure 3 (inset) shows three of these periodic arrangements of holes in isotopically pure $^{12}$C graphene, where single [cases (a) and (b)] or pairs [case (c)] of carbon rings have been removed at each hole. It should be noted that these are the initial configurations of the carbon atoms. The corresponding PnDOS, after the relaxation of the lattice, are shown in Fig. 3. Besides the fact that the major features appearing in the PnDOS of graphene, as described earlier, seem to be smoothed out by the introduction of defect holes, there are no PBGs. Another type of vacancies discussed in the literature is the removal of pairs of neighboring carbon atoms. Examining several periodic arrangements of this type of holes (see for example Fig. 4, inset), Fig. 4 shows that these vacancies do not introduce PBGs in the PnDOS either. It seems that these defects tend to preserve the initial features of the graphene’s PnDOS. Other type of defects, such as blisters, and the addition of single or pairs of carbon atoms do not create any detectable PBGs in the PnDOS (data not shown).

Gaps appear in the PnDOS of graphene when, using the same periodic configuration as the one shown in the inset of Fig. 1, half of the carbon atoms are replaced by silicon atoms (a configuration referred from here on as SiC graphene). Figures 5(a) and 5(b) show the SiC phonon dispersion curves and the PnDOS calculated by first principles calculations, respectively. From Fig. 5 it is evident that an energy gap appears between 670 and 840 cm$^{-1}$, while the highest phonon frequency is located at $\sim$1070 cm$^{-1}$. The gap over midgap ratio ($\Delta\omega/\omega_g$) is about 0.225. The high energy modes ($>840$ cm$^{-1}$) come from the TO and LO branches. In pure graphene the LA branch overlap with LO and TO branches particularly in the K-M direction of the Brillouin zone. In contrast, for SiC graphene a clear gap between the optical
and LA branches is observed (Fig. 5(a)). The PnDOS peak of SiC at about 620 cm$^{-1}$ comes exclusively from the LA phonon branch. Similar calculations for germanium replacing carbon atoms in graphene resulted in a PnDOS with two phonon energy gaps.26 The lower one is between 380 and 490 cm$^{-1}$ ($\Delta\omega/\omega_0 = 0.253$) while the higher and narrower gap appears between 610 and 700 cm$^{-1}$ ($\Delta\omega/\omega_0 = 0.137$). It is clear that replacing carbon atoms in graphene with other higher atomic mass atoms favors the creation of phononic band gaps. This is reminiscent to that encountered in higher dimensional phononic crystals, where larger mass density contrast favors the opening of band gaps.27

At this point, it is important to mention that the chemical substitution of graphene is a newly established research field, developed in order to modify its electronic, mechanical, and optical properties. Boron and nitrogen are the best candidates that could substitute carbon atoms since these elements are the carbon’s neighbors in the periodic table. Nitrogen has been already experimentally explored as an effective dopant for graphene.32–34 Boron substitutional doping has significant effects on the graphene structure, namely it introduces chemical disorder since the B–C bond is 0.5% longer than the C–C bond.35 Concerning silicon and germanium defects in graphene crystal lattice, there are only theoretical studies in the literature at the moment, focused mainly on the concomitant electronic band structure modifications.36 There are also theoretical studies predicting stable two dimensional honeycomb structures of silicon and germanium.37

The PnDOS of SiC graphene obtained from the MD simulations (solid line in Fig. 6) has also a gap between 490 and 600 cm$^{-1}$, while the highest frequency phonon appears at 845 cm$^{-1}$. The gap has $\Delta\omega/\omega_0 = 0.234$ which agrees well with the corresponding value from the ab initio calculations. However, the features in the MD PnDOS are always at lower frequencies relative to the corresponding features in the ab initio PnDOS by 20%-28%.

Substituting 50% of the carbon atoms in graphene with silicon atoms and keeping the ordered arrangement shown in the inset of Fig. 1, it may be difficult to be achieved experimentally. For that reason, the effect of disorder in that configuration was studied. By randomly interchanging 5% of carbon and silicon atoms with the other type of atoms (silicon and carbon, respectively) but keeping the total number of both atoms equal (50% of each species), the PnDOS inside the band gap region acquires a finite value (see dash line in Fig. 6). This can be attributed to the creation of localized states inside the phononic band gap that appear at the edges of the gap and as the disorder increases they occupy the whole band gap region. Phonon states also appear above 845 cm$^{-1}$ (the cut-off frequency for the periodic SiC configuration), since the PnDOS has a non zero value in that region. Increasing the disorder further, more phonon states appear in frequencies above 845 cm$^{-1}$ and inside the band gap. In general, the sharp peaks in the PnDOS of ideal SiC graphene, tend to disappear as the disorder increases. Nevertheless, even at 50% disorder (dotted-dash line in Fig. 6), there is a PnDOS minimum at around 550 cm$^{-1}$, the remnant of the band gap of the periodic case.

Snapshots of single realizations’ evolution of such graphene layers (with 50% carbon and silicon atoms) after 30000 MD time steps for 5% and 25% disorder are shown in Fig. 7. For 5% disorder, there are no significant changes in the location of the atoms except for the atoms at the edges (we remind that free boundary conditions are used). However, for the 25% disorder, there are areas with atoms clearly away from the graphene layer even at the center of the structure. This happens when two or more silicon atoms become neighbors. Since their bond lengths are higher than Si–C and especially C–C bond lengths, some of those Si atoms are forced outside the graphene layer.

Furthermore, states inside the gap of the periodically arranged SiC graphene appear also when the temperature rises, as it can be seen from Fig. 8(a). In particular the PnDOS at 545 cm$^{-1}$ (the midgap frequency for MD simulations at 300 K) is $0, 10^{-5}, 0.7 \times 10^{-4}, 1.2 \times 10^{-4} 1/cm^{-1}$, for $T = 300, 600, 900, 1200 K$, respectively. The PnDOS at the edges of the gap increases even more as the temperature rises, while the upper energy gap edge moves towards the lower frequencies (see Fig. 8(a)). Similarly, the highest frequency phonon moves to lower frequencies as the temperature rises (it appears at 845, 835, 822, and 816 cm$^{-1}$ for

![FIG. 6. PnDOS obtained from MD simulations of SiC graphene, where half of graphene’s carbon atoms are periodically replaced by silicon with the same arrangement as in the inset of Fig. 1 (solid line). Dash, dotted, and dotted-dash lines correspond to the cases where 5%, 25%, and 50%, respectively, of the carbon (silicon) atoms in SiC are randomly interchanged with silicon (carbon).](image-url)

![FIG. 7. Snapshots of the configuration of the atoms after 30000 MD time steps for the cases described in Fig. 6 with 5% [(a) and (b)] and 25% [(c) and (d)] disorder. Views are shown from the top in (a) and (c) and from the side in (b) and (d).](image-url)
significant drop in PnDOS at around 945 cm$^{-1}$ corresponding to optical modes. The 4/16 Si case (solid line in Fig. 9) has a pronounced PnDOS peak at about 730 cm$^{-1}$. The inset of Fig. 9 shows the temperature dependence of the high energy peak at about 730 cm$^{-1}$.

$T = 300$, 600, 900, and 1200 K, respectively). The inset of Fig. 8(a) shows the temperature dependence of the pronounced PnDOS peak at about 730 cm$^{-1}$ corresponding to optical modes. A considerable softening at a rate of $-0.047$ cm$^{-1}$/K is clearly manifested from the inset of Fig. 8(a). It is important to mention that this value represents a rough estimate of the optical mode softening, ignoring completely the interactions of phonons with the electronic system. For comparison, the PnDOS of single layer graphene (with only carbon atoms) is depicted in Fig. 8(b). In this case, due to the appearance of many peaks in the high energy region, it is not safe to extract temperature dependencies for the optical modes.

Additionally, the phonon band gaps in the PnDOS of graphene with silicon impurity atoms depend on the composition and the arrangement of the atoms. Figure 9 shows three different compositions and arrangements of periodic structures having 10/16 Si atoms (6/16 C atoms), 6/16 Si (10/16 C), and 4/16 Si (12/16 C). In these cases, we construct a periodic arrangement of atoms using suitable supercells as shown in Fig. 9 and perform MD simulations, as described earlier, in order to obtain the final configurations and extract the corresponding PnDOS. The 4/16 Si case (solid line in Fig. 9) has a significant drop in PnDOS at around 945 cm$^{-1}$ and another one at 720 cm$^{-1}$. The highest phonon frequency is at 1360 cm$^{-1}$. The 6/16 Si case (dash line in Fig. 9) exhibits a wide gap from 880 to 1090 cm$^{-1}$ ($\Delta \omega /\omega_g = 0.213$), another drop at 625 cm$^{-1}$, whereas the highest frequency phonon is at 1260 cm$^{-1}$. Finally, the 10/16 Si case (dotted line in Fig. 9) has a single well defined band gap between 435 and 610 cm$^{-1}$ ($\Delta \omega /\omega_g = 0.335$), and the highest phonon frequency at 780 cm$^{-1}$. Therefore, by increasing the number of Si relative to the C atoms, the band gap over midgap ratio in the PnDOS increases in the examined cases. This result is in accordance with a recent $ab$ initio study concerning Ge substitutions in graphene. In the latter study, the 10/16 Ge composition gave the widest band gap with $\Delta \omega /\omega_g = 0.598$.

CONCLUSIONS

The phonon density-of-states of graphene with various types of defects was calculated using both first principles and molecular dynamics simulations. The theoretical findings reveal that removing or adding carbon atoms in graphene does not create any band gaps in the PnDOS. Also, replacing half of the $^{12}$C atoms with $^{14}$C does not create band gaps either. However, the periodic replacement of half of the carbon atoms with silicon ones introduced sizable band gaps in the PnDOS. These gaps become wider as 10 out of 16 carbon atoms are replaced with silicon, in periodic structures. Comparing $ab$ initio and semiempirical MD simulations, there is a systematic shift of the band gaps and other features in the PnDOS towards the lower frequency for the MD cases. This shift is about 5%-8% for the pure carbon cases and increases to 20%-28% for the C-Si cases. It has to be pointed out here the huge difference in computation time and memory requirements between the two calculations. The $ab$ initio simulations take several hours to a day for a unit cell of 16 atoms. Similar MD simulations for 1248 atoms take a few minutes. Finally, MD simulations for disorder and higher temperatures showed that the band gaps tend to disappear as they gradually filled up with localized states.