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N. Singh, T. P. Kaloni, and U. Schwingenschlögl

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A first-principles investigation of the optical spectra of oxidized graphene

N. Singh,a) T. P. Kaloni, and U. Schwingenschlögla)

Physical Science and Engineering Division, KAUST, Thuwal 23955-6900, Kingdom of Saudi Arabia

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The electronic and optical properties of monoxide, di, tri, and tetravacancies in graphene are studied in comparison to each other, using density functional theory. In addition, oxidized monovacancies are considered for different oxygen concentrations. Pristine graphene is found to be more absorptive than any defect configuration at low energy. We demonstrate characteristic differences in the optical spectra of the various defects for energies up to 3 eV. This makes it possible to quantify by optical spectroscopy the ratios of the defect species present in a sample. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4781382]

While graphene is a zero band gap material, a finite band gap is needed for various applications aiming at graphene-based electronic devices.1,2 Functionalization is one of the possible methods to open a band gap, for example, by simple oxidation.3,4 Graphene oxide (GO) with epoxy, carbonyl, or hydroxyl groups could enable tuning of the band gap and, therefore, tailoring of the electronic, mechanical, and optical properties.6,7 The atomic structure of GO has been studied experimentally8,9 and theoretically.10 In addition, the stability of GO has been analyzed by first principles calculations in Ref. 11. Using the same approach, the adsorption of nitrogen on graphene and GO has been addressed in Ref. 12, and the mechanical properties of both ordered and amorphous GO have been investigated in Ref. 13. Recently, GO nanostructures have received a lot of attention due to the fact that they pave the way to solution based synthesis of graphene, low cost, easy processability, and compatibility with various substrates.14 The band gap of GO can be tuned just by varying the oxidation level. Full oxidation leads to an electrical insulator, while partially oxidized GO is rather a semiconductor.15 Moreover, experiments demonstrate that GO nanostructures are promising for applications in photocalysis.16 Reduction of GO enables graphene mass production.17

A controlled deoxidation of GO leads to an electrically and optically active material that is transparent and conducting. Furthermore, in contrast to pristine graphene, GO is fluorescent over a broad range of wavelengths, owing to its heterogeneous electronic structure.15 It can contain different chemical compositions of carbon, oxygen, and hydrogen.8,18 While commonly epoxy and hydroxyl groups are found, there can also be small contributions of carbonyl and carboxyl groups. Experimentally, a coverage between 25% and 75% has been observed, reflecting that typically a quarter of the C–C bonds are double bonds whereas the other are single bonds.19 The adsorption behavior of oxygen atoms on graphene has been studied by first-principles calculations, demonstrating that the lattice constant increases with the O/C ratio because of the formation of epoxy groups. At an O/C ratio of 50%, a finite band gap of 3.39 eV is found.20

Attachment of a carbonyl group leads to an almost planar sp2 electronic configuration because the formation of C–O bonds induces little strain in the graphene sheet. On the contrary, attachment of an epoxy group leads to a non-planar distorted sp3 electronic configuration for those carbon atoms which are connected to oxygen. This process creates a significant strain on neighboring C–C bonds.17 The combination of sp3 and sp2 configurations (confirmed experimentally21 and theoretically17) as well as defects breaks the hexagonal symmetry of pristine graphene, and a band gap is opened. Furthermore, the defects associated with dangling bonds enhance the reactivity substantially.22

A theoretical investigation of the electronic and optical properties of GO (without vacancies) for different functional groups and various compositions has been reported in Ref. 4. The authors found that carbonyl groups are favourable for photoluminescence and that the optical gap of reduced GO is smaller than that of pristine and fully oxidized graphene. Experimental and theoretical studies23,24 indicate that hydroxyl, carboxyl, and other functional groups can more easily be attached to vacancies in graphene than to pristine graphene. Therefore, a study of the electronic and optical properties of defective GO becomes critical. The optical properties of oxidized mono, di, tri, and tetravacancies in graphene have not been reported so far. In this work, we use first-principles calculations to provide insight into this topic.

Our calculations are based on density functional theory and carried out using the generalized gradient approximation25 (Quantum-ESPRESSO package26). All calculations are performed with a plane wave cutoff energy of 544 eV. We employ a Monkhorst-Pack27 8×8×1 k-mesh for the Brillouin zone integration in order to well relax the structures and achieve a highly accurate electronic structure. A 5×5 supercell of graphene is sufficiently large for describing monovacancies and oxidized monovacancies.5 Our supercell has an in-plane lattice constant of a = 12.2 Å and extends c = 20 Å in the perpendicular direction. It has been reported that nearby vacancies behave independently when they are separated by ~7 Å.28 Hence, we use a 6×6 supercell for describing di, tri, and tetravacancies to avoid artificial interaction of the periodic images. This supercell has an in-plane lattice constant of a = 14.69 Å, and we choose again c = 20 Å. The cell parameters and atomic positions are fully relaxed until force convergence of 0.05 eV/Å and energy

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a)Electronic mail: nirpendra.singh@kaust.edu.sa.
b)Electronic mail: udo.schwingenschlogl@kaust.edu.sa.
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convergence of $10^{-7}$ eV are reached. The relaxed structures are used to calculate the optical properties by means of the WIEN2k code. This code has been successfully applied to narrow band gap materials including rare earth Zintl compounds and oxides. For a reliable integration, a set of 180 k-points in the irreducible wedge of the Brillouin zone is employed. A Lorentzian broadening is used to simulate the effects of finite life-time and finite resolution in optical measurements.

The dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ describes the optical response. The imaginary part is calculated by summing all transitions from occupied to unoccupied states over the Brillouin zone, weighted with the matrix element giving the probability of a transition. Then the real part is given by the Kramers-Kronig relation. The reflectivity spectra are derived using the Fresnel formula for normal incidence, assuming an orientation of the crystal surface parallel to the optical axis: $R(\omega) = |(\sqrt{\varepsilon(\omega) - 1})/\sqrt{\varepsilon(\omega) + 1}|^2$. Moreover, the dielectric function determines the optical absorption $\alpha(\omega) = \sqrt{2}\omega\sqrt{\varepsilon(\omega)} - \varepsilon_1(\omega)$, the real part of the optical conductivity $\sigma_\text{Re}(\omega) = \omega\varepsilon_2(\omega)/4\pi$, and the electron energy loss function $L(\omega) = \varepsilon_2(\omega)/|\varepsilon(\omega)|^2$.

The calculated formation energies of mono, di, tri, and tetravacancies in graphene are 7.5 eV, 6.9 eV, 11.5 eV, and 12.6 eV, respectively. This means the formation of a divacancy is more favourable than the formation of a monovacancy. Furthermore, a divacancy is known to be more stable than two isolated monovacancies (which have a rather low migration energy barrier), because an octagon is formed in which the dangling C–C bonds passivate each other.

Mono, tri, and tetravacancies turn out to induce ferromagnetism with total magnetic moments of 1.35 $\mu_B$, 1.00 $\mu_B$, and 2.00 $\mu_B$, respectively, whereas divacancies show no spin-polarization because the dangling bonds are passivated. The results of our band structure calculations for non-oxidized vacancies are shown in Fig. 1, together with the corresponding density of states. In the 6 x 6 supercell, the Dirac cone is shifted to the $\Gamma$-point due to Brillouin zone folding. In case of the tetravacancy, the band structure shows that a single minority spin band crosses the Fermi energy (near the $\Gamma$-point) and leaves the system metallic, whereas for the di and trivacancies both spins contribute at the Fermi energy. Moreover, an upward shift of the Dirac point is indicative of a hole-doped system. Since in the case of the divacancy the density of states shows spin degeneracy, a non-magnetic metallic state is established. For an oxidized monovacancy, the magnetic and electronic properties have been reported previously.

Optical spectroscopy is a powerful tool in materials science to learn about local structural properties. Our calculated optical spectra of pristine graphene and its functionalized derivatives are summarized in Fig. 2. We note that in these results, self-energy and excitonic effects are not taken into account. However, it has been demonstrated for graphene that for energies up to 3 eV the influence of many particle effects is negligible. The optical spectra show that for two adsorbed oxygen atoms a band gap of 0.5 eV is opened due to the symmetry breaking and increased $sp^3$ character of the carbon states. A semiconducting behaviour is confirmed for this configuration by previous calculations of the band structure and density of states. In contrast, all non-oxidized...
defects under investigation are found to create metallic states, which are demonstrated in Fig. 1.

The optical spectra in general are found to exhibit very characteristic features for the different defects, which highlight a high sensitivity of optical spectroscopy for determining the defect type. Pristine graphene is more absorptive than the other systems under consideration, except close to 3 eV where a high absorption is found for the monovacancy with two adsorbed oxygen atoms. For the divacancy and for three adsorbed oxygen atoms at the monovacancy pronounced peaks evolve around 1.3 eV (visible region). For all the systems under investigation the peaks in the optical spectra are mainly attributed to $\pi-\pi^*$ transitions of the aromatic carbon atoms. The absorption peaks around 0.5 eV are related to unsaturated dangling bonds, which appear in the cases of the mono, tri, and tetravacancies. On the other hand, the peaks

FIG. 2. Optical absorption $\alpha(\omega)$ in $10^4$ cm$^{-1}$, optical conductivity $\sigma(\omega)$, reflectivity $R(\omega)$ in %, and energy loss function $L(\omega)$ of pristine graphene, as compared to graphene with (oxidized) mono, di, tri, and tetravacancies.
around 1.3 eV originate from the formation of carbon penta
gon structures. Pristine graphene shows the highest reflectiv-
ity at low energy. In addition, the reflectivity is higher for
the tetravacancy than for the mono, di, and trivacancies,
because here the metallicity is most pronounced. The low
energy reflectivity is lowest for the monovacancy with two
adsorbed oxygen atoms, due to the semiconducting nature of
this system and increases for three and four adsorbed oxygen
atoms.

In conclusion, we have studied the optical properties
of graphene derivatives (clean and oxidized vacancies) by
means of density functional theory. We find that the for-
mation of divacancies in graphene is energetically favour-
able. Divacancies are also exceptional in the sense that
they do not lead to a local magnetic moment. Mono, di,
tri, and tetravacancies are found to be metallic, while an
oxidized monovacancy with two adsorbed oxygen atoms
leads to a band gap of 0.5 eV (due to a splitting of the
Dirac cone). Our optical spectra show that pristine gra-
phene has the highest absorption in the energy range
below 2.5 eV. In two cases (tetravacancy and monova-
cancy with three adsorbed oxygen atoms) a prominent
absorption peak appears in the visible range. Our calcula-
tions suggest that the types of (oxidized) defects present in
a graphene sample can be quantified by optical spectro-
copy. With this knowledge, the electronic and optical
properties of graphene derivatives can be tuned by con-
trolled oxidation and reduction.

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