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PAPER

Oxidation of monovacancies in graphene by oxygen molecules

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We study the oxidation of monovacancies in graphene by oxygen molecules using first principles calculations. In particular, we address the local magnetic moments which develop at monovacancies and show that they remain intact when a molecule is adsorbed such that the dangling carbon bonds are not fully saturated. However, the lowest energy configuration does not maintain dangling bonds and is found to be semiconducting. Our data can explain the experimentally observed behavior of graphene under exposure to an oxygen plasma.

I. Introduction

Graphene is formed by a two dimensional layer of carbon atoms which have a hexagonal crystal symmetry.¹ Great interest in this material arises from its unique electronic and optical properties, combined with potential technological applications, *e.g.* in spintronics. Induced magnetic moments in carbon systems have been confirmed theoretically for various cases: vacancies in graphene, graphite, and diamond,^{2,3} vacancies with adsorbed hydrogen in graphite,^{4,5} hexagonal defects in graphene and carbon nanotubes,⁶ and adsorption of molecular oxygen and hydrogen on graphene.^{7,8} Recently, a transition from metallic to semiconducting behavior has been observed for single layer graphene after exposure to an oxygen plasma.⁹ This aging mechanism, which is of particular technological importance, has been attributed to oxygen decoration (*i.e.* single oxygen atoms are placed midway above C–C bonds). However, such a model cannot explain simultaneous indications of a p-type state.⁹ It consequently seems likely that the metal-semiconductor transition is related to modifications of magnetic vacancies. In this context, we study the oxidation of graphene by oxygen molecules by means of first principles calculations. We will show that this oxidation mechanism already allows us to explain the origin of the metal-semiconductor transition as well as the p-type state. In addition, we clarify the prerequisites and the mechanism leading to the formation of local magnetic moments at oxidized monovacancies in graphene.

II. Computational methods

We employ density functional theory¹⁰ in the generalized gradient approximation as implemented in the plane wave Quantum

Espresso code.¹¹ This code has already been applied successfully to graphene in various instances.^{12–17} Perdew–Burke–Ernzerhof norm-conserving pseudopotentials are employed.¹⁸ All calculations are performed with a plane wave cutoff energy of 544 eV. We have compared different k-meshes and values of the smearing in order to check for convergence. A Monkhorst–Pack¹⁹ scheme with a $8 \times 8 \times 1$ k-mesh for the Brillouin zone integration turns out to be sufficient to relax the crystal structure and to calculate the band structure.²⁰ However, a $16 \times 16 \times 1$ k-mesh is used for calculating the density of states (DOS) in order to obtain a high resolution at the Fermi energy (E_F). We find that a 5×5 supercell of pristine graphene is sufficiently large for our calculations. This supercell contains 50 carbon atoms and has a lattice constant of $a = 12.2$ Å. Interlayer interactions due to the periodic boundary conditions is prevented by a vacuum slab of about 20 Å thickness. The atomic positions and cell parameters are fully relaxed in all cases, until an energy convergence of 10^{-7} eV and a force convergence of 0.05 eV Å⁻¹ is reached. In a first step, we create a monovacancy in our 5×5 supercell and relax the system. Then we add an oxygen molecule close to the monovacancy, where we use different starting geometries, and afterwards relax the system again. Six prototypical structures are discussed in the following.

III. Results and discussion

The structural optimization of the supercell with the monovacancy, see configuration V in Fig. 1, shows that the atoms C1 and C2 are displaced from their initial positions, giving rise to a pentagonal structure similar to that reported in ref. 21. The interatomic distance between C1 and C2 amounts to 2.38 Å, between C2 and C3 to 2.50 Å, and between C1 and C3 to 2.51 Å. In configurations V1 and V2, which are equivalent by symmetry, the two atoms of the oxygen molecule are located on the same side of the graphene sheet, whereas they are located on opposite sides in configurations V3 and V4. Under our configurations, V4 has the lowest energy. In this case we have C3–O2 and C1/C2–O1 bonding above and below the graphene sheet, respectively. For the pristine monovacancy the carbon atoms form an almost ideally flat sheet.

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Fig. 1 Crystal structure before and after the relaxation.

After oxidation, however, the system is locally distorted since the adsorbed oxygen atoms force the nearest and next nearest neighbour carbon atoms to move perpendicular to the graphene sheet.

We determine the formation energy:

$$E_{\text{formation}} = E_{\text{vacancy}+\text{O}_2} - E_{\text{vacancy}} - 2E_{\text{O}}$$

where $E_{\text{vacancy}+\text{O}_2}$ is the total energy of our supercell with two oxygen atoms attached to the monovacancy, E_{vacancy} is the total energy of the pristine monovacancy, and E_{O} is the total energy of an isolated oxygen atom. The calculated values of the formation energy $E_{\text{formation}}$ are -13.76 eV and -17.44 eV for configurations V1/V2 and V3/V4, respectively. These values show that oxygen doping of defective graphene is a favourable reaction. It is in fact more favourable than oxygen doping of pristine graphene, since defective graphene contains reactive dangling bonds. It is known that temperature and oxygen partial pressure have a strong impact on the reaction thermodynamics of the vacancy oxidation in graphene.²² However, for our following line of reasoning it is important to note that the energetic order of the configurations V1/V2 and V3/V4 will not be inverted. We find magnetic solutions for configurations V1 and V2, in which one carbon bond remains unsaturated. In contrast, configurations V3 and V4, in which all dangling bonds are saturated, turn out to show no spin polarization. The total energy difference per supercell between

the magnetic and the non-magnetic cases, $\Delta E = 3.68$ eV, stresses that the non-saturated configurations V1 and V2 are considerably less stable than the saturated configurations V3 and V4, due to the dangling bonds.

We have performed a band structure calculation for the monovacancy along the Γ -K-M- Γ path. The result is shown in Fig. 2 (configuration V) together with the corresponding DOS. In addition, a charge density map is given in Fig. 3. Close inspection of the band structure shows that two bands (one spin up and one spin down band) cross E_{F} , leaving the system metallic. These two bands are part of the π bands arising from C-C bonding. The obtained DOS confirms a significant spin polarization induced by the monovacancy. We find a sharp DOS peak at E_{F} due to

Fig. 2 Electronic bands along the path Γ -K-M- Γ (left) and density of states (right) of a pristine vacancy (V) and of vacancies decorated with two O atoms (V1 and V4).

Fig. 3 Charge density in configurations V, V1, and V4.

rather flat bands, which points at Stoner band magnetism.²³ The calculated magnetic moment of $1.35 \mu_B$ is consistent with the value of ref. 3.

We next deal with the reaction between an oxygen molecule and the monovacancy. To this aim, we place the molecule in different prototypical positions and allow the structure to relax. Configurations V1 and V2 turn out to be magnetic. In the case of configuration V1, bonds form between the atoms C1 and O1, see Table 1, and between C2 and O2. For configuration V2, bonds form between C1 and O1 and between C3 and O2. In both these cases the two oxygen atoms are located on the same side of the graphene sheet. The calculated C–C and C–O bond lengths are given in Table 1. In configuration V1 the sp^2 dangling bonds of C1 and C2 are saturated (independently) by the oxygen atoms O1

Fig. 4 Spin density in configurations V, V1, and V4.

and O2. In contrast, the dangling bond of atom C3 remains unsaturated and magnetism is induced. We observe a total magnetic moment of $1.86 \mu_B$, contributed mainly by the free electron of atom C3, see the corresponding spin density map in Fig. 4. The electronic structure of configuration V1 is addressed in Fig. 2. Similar results are obtained for configuration V2 and therefore not shown. From the band structure it is clear that a single (spin up) band crosses E_F at the K-point and leaves the system metallic. Moreover, the evident splitting and upward shift of the Dirac cone is indicative of a p-type state, similar to the pristine monovacancy.

The spin density distribution around the vacancy site, as shown in Fig. 4, confirms the conjecture that the magnetic moment can be attributed to atom C3. However, the fact that the moment is

Table 1 Selected C–C and C–O bond lengths (in Å)

	C1–C2	C1–C3	C2–C3	C1–O1	C1–O2	C2–O2	C3–O1	C3–O2	C2–O1	O1–O2
V1	3.05	2.87	2.87	1.23	3.00	1.23	3.02	3.04	2.99	2.45
V2	2.87	3.05	2.87	1.23	3.00	3.02	2.99	1.23	3.02	2.45
V3	2.87	2.34	2.34	2.45	1.43	2.45	1.53	1.53	1.43	2.27
V4	2.40	2.96	2.96	1.39	3.04	3.04	2.28	1.23	1.39	2.67

larger than $1 \mu_B$ shows that also the delocalized π -states become polarized. We note that the area around the monovacancy is similar to a zigzag graphene nanoribbon, which can be transformed from a nonmagnetic semiconductor to both a metal and a magnetic semiconductor by increasing its length.²⁴ Divacancies in graphene counteract magnetism due to the formation of two carbon pentagons.²⁵ For an even number of vacancies both spin polarized and non-polarized cases have been reported, while magnetism is maintained for an odd number of vacancies.

When the oxygen atoms saturate all dangling bonds we obtain no spin polarization and the lowest total energy. In configuration V4, there is bonding between C3 and O2 above and between C1/C2 and O1 below the graphene sheet. The situation is similar for configuration V3 in which we have bonds between C1/C3 and O2 above and between C2/C3 and O1 below the graphene sheet. The calculated C–C and C–O bond lengths are summarized in Table 1. In Fig. 2 (configuration V4), we address the electronic structure. For configuration V3 the results are similar and consequently not shown. We find that a band gap of about 0.5 eV is opened, due to a splitting of the Dirac cone. The free C1, C2, and C3 electrons get involved in bonding with the oxygen atoms, forming one C–O–C bridge and one carbonyl (C=O) group. Hence, no spin polarization is induced, which is confirmed by the DOS. We conclude that it depends on the adsorption site and chemical bonding whether a monovacancy stays metallic or becomes semiconducting under oxygen adsorption.

In Fig. 5 we address the spin polarization by means of the atomic charges deduced from a Löwdin population analysis. The quantities ΔC and ΔO are defined as the differences of the spin up and spin down charges (measured in units of electrons) at the different C and O sites, respectively. The data indicate that a monovacancy in graphene induces a finite spin polarization (see the left hand side of Fig. 5). The values in the central column of Fig. 5 for the case of configuration V1 show that bonding to the oxygen atoms results in a significant charge redistribution, which in the end leads to a remarkable magnetic moment of $0.82 \mu_B$ on the C3 atom. For configuration V4 there is no spin polarization observed.

Finally, there remains the question whether the two characteristic behaviors represented by configurations V1 and V4 will change under further oxidation.²⁶ To this aim, we have added more oxygen atoms to our supercells and have relaxed the structures analogously to the procedure described before. The resulting band structures are presented in Fig. 6 and the relaxed crystal

Fig. 5 Löwdin population analysis for configurations V and V1.

Fig. 6 Electronic bands along the path Γ -K-M- Γ (left) and density of states (right) after further oxidation of configurations V1 and V4, i.e. decoration with three and four O atoms (from top to bottom).

Fig. 7 Relaxed crystal structure for decoration with three and four O atoms.

structures in Fig. 7. The formation energies of -20.44 eV and -23.23 eV for configuration V1 after decoration by a third and a fourth oxygen atom, respectively, show that a further oxidation is energetically favorable. The same is true for configuration V4, for which we calculate formation energies of -21.85 eV and -26.17 eV. Turning to the electronic properties, we obtain for configuration V1 reduced magnetic moments of $1.69 \mu_B$ and $1.25 \mu_B$ in the case of decoration with three and four oxygen atoms. Configuration V4, in contrast, does not develop spin polarization for any decoration. For comparison with Fig. 2, analogous plots of the band structure and DOS are shown in Fig. 6 for decoration with three and four oxygen atoms. We can conclude that for both cases, V1 and V4, only gradual alterations from the results for reaction with an oxygen molecule appear. In particular, the magnetic metallic nature of configuration V1 and the non-magnetic semiconducting nature of configuration V4 are maintained, the latter being lower in energy.

IV. Conclusion

In conclusion, we have studied a monovacancy in graphene which interacts with molecular oxygen. The electronic structure and magnetic properties have been calculated by means of density functional theory. A magnetic moment of $1.35 \mu_B$ is observed for the monovacancy, contributed mainly by the free electron of carbon atom C3, see Fig. 4. The total magnetic moment with adsorbed oxygen is found to be $1.86 \mu_B$ if only C=O double bonds are formed. In contrast, there is no magnetic moment if at least one C–O–C bridge is formed. This can be explained by the fact that the magnetism traces back to the dangling carbon bonds. We observe p-type states both for the pristine monovacancy and for specific oxidized monovacancies. For the energetically most stable configuration, however, we obtain a transition into a non-magnetic semiconducting state. More generally speaking, the vacancies are found to be magnetic if and only if they are metallic and non-magnetic if and only if they are semiconducting. Metallicity and magnetism are simultaneously determined by the presence or absence of dangling carbon bonds after the oxidation. For this reason, the formation of magnetic moments depends on the kinetics of the reaction path. It therefore is to be expected that also metastable oxidized vacancies with a finite magnetic moment are present in real samples, in agreement with the observations reported in ref. 9. A

further reaction path analysis should be performed in order to shed further light on this issue.

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