Structural bistability of the oxygen-adsorbed graphene sheet

J Nakamura, J Ito and A Natori

Department of Electronic-Engineering, The University of Electro-Communications (UEC-Tokyo), 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan

E-mail: junj@ee.uec.ac.jp

Abstract. Structural and electronic properties for oxygen-adsorbed graphene sheets have been explored using first-principles total-energy calculations within the local spin density functional theory. It has been found that the structural bistability appears with regard to the oxygen adsorption. This bistability corresponds to the formation of epoxy group or ether group, where the ether group phase is more stable than the epoxy group one. Further, the relative stability for the one-side adsorption model to the both-sides one is explored; oxygen atoms prefer to adsorb on both sides of the graphene sheet, while the one-side adsorption structure becomes metastable.

1. Introduction

Oxidation is the basic and important process for the carbon-based materials as an initial process of purification, for example, for producing very thin graphitic materials composed of a single or several graphene layers [1, 2]. Horiuchi and co-workers have prepared carbonfilms with nanometer-thicknesses starting from the oxidation of graphite, which are referred to carbon nanofilms (CNF) [1, 2]. They have reported that the electronic conductivity of CNF changes from insulative to semiconducting after heating, while graphite and graphite oxide are a semimetal and a insulator, respectively. It has been also reported that the electrical conductivity of graphite oxide can be significantly increased by chemical reduction [3, 4, 5, 6]. Then, it is expected that the difference of electrical property is lead by interaction between graphite and oxygen atoms.

Recently, it has been reported that the epoxy group on the graphene breaks carbon-carbon bonds, followed by the formation of ether groups [7, 8, 9]. Such ether groups tend to align one-dimensionally, resulting in the introduction of cracks in graphite. Before turning to the dynamics of the reaction of oxygen atoms with graphite, we have to clarify energetics and cohesive properties for the adsorption of oxygen atoms on the graphene surface. In this study, we give the investigation of the structural and electronic properties of oxygen-adsorbed graphene sheet using first-principles total-energy electronic-structure calculations within the local spin density functional theory.

2. Models and calculations

We considered a model in which the oxygen atoms are adsorbed at the bridge sites on the graphene [10, 11] with a coverage of 50% (C_2O), as shown in Fig. 1. We assumed the so-called epoxy group was formed initially at each adsorption site in this geometry, since the epoxy group
is deemed to a precursor for the oxygen reaction on the graphene sheet. It has been reported in Ref. 7 that ether groups on the graphene fragment can be stabilized if the oxygen aligns linearly. In order to clarify the relative stability between epoxy and ether groups on the graphene sheet, we calculated the total energy of this system as a function of the oxygen height above the basal plane of the sheet, accordingly as a function of the lateral length of the unit cell, \( a \), as indicated in Fig. 1. The optimized lattice constant for graphene (\( a=4.24 \) Å) agrees well with the experimental value for graphite, 4.26 Å. We have considered the both-sides adsorption model as shown in Fig. 1(c) as well as the one-side adsorption model (Fig. 1(b)) for comparison. A supercell geometry was used with a large separation (15 Å) between the sheet in order to decouple each graphene layer.

We used first-principles total energy calculations [12, 13, 14] on the basis of the density functional theory [15]. A local (spin) density functional given by Perdew and Wang [16] was utilized as the exchange-correlation energy functional. The ultrasoft pseudopotentials generated by the Vanderbilt strategy [17] were adopted. The wave functions were expanded in a plane-wave basis set with the kinetic-energy cutoff of 36 Ry. Structural optimization was performed until each component of the interatomic force became less than \( 1 \times 10^{-3} \) Hartree/\( \text{a.u.} \).

### 3. Results and discussion

Figure 2(a) shows adsorption energy of an oxygen atom on the graphene sheet as a function of the unit-cell length as shown in Fig. 1. Here, we have optimized the atomic configuration for the given unit-cell length \( a \), starting from \( a=4.24 \) Å. Interestingly, the adsorption energy curve has two minima, indicating that the system is bistable. In Fig. 2(b), change of the length of the C-C bond located just beneath the oxygen atom is shown. It is clearly seen that the C-C bond length changes discontinuously at \( a=4.8 \) and 5.6 Å for the both-sides and the one-side models, respectively. These discontinuous changes of the bond length are indicative of the breaking of the C-C bond, that is, the transition of the bond configuration from the epoxy group to the ether one. Thus, double minima in energy shown in Fig. 2 correspond to the different structural phases: one is the epoxy group and the other is the ether one. Optimized atomic arrangements of (meta-)stable phases for the one-side and the both-sides model are shown in Figs. 2(c) and 2(d), respectively. Furthermore, we can see the both-sides model is more stable than the one-side model as seen in Fig. 2. The main reason is that the strain in the basal plane of graphene is efficiently reduced in the both-sides configuration; each oxygen atom serves as a hinge in the folding structure, see (iv) in Fig. 2(d).

Next, we explore the energy barrier for the conformation change between both-sides and
Figure 2. (a) Adsorption energy per one oxygen atom and (b) length of the C-C bond located just beneath the oxygen atom for the one-side model (red circle) and for the both-sides model (green square), as a function of the unit-cell length shown in Fig.1. In this study, the lattice constant along the oxygen row was fixed to $b=2.45$ (bulk value). Energy of the most stable structure for the ether phase of the both-sides model, is set to be zero. Atomic configurations for the one-side adsorption model (c) and for the both-sides adsorption model (d).

Figure 3. (a) Energy variation for the structural change between the one-side and both-sides adsorption models, as a function of the z-coordinate of the oxygen atom indicated as "O1" in Fig.3(b). (b) Initial structure where an oxygen atom is located at $z=0$ (one-side model for the ether group). Directions of pushing down and pulling up are also indicated in Fig. 3(b). Resulting most stable structures (both-sides model (A) ($z=-1.1$ Å) and (B) ($z=+0.3$ Å) are shown in Fig. 3(c).
one-side adsorption. Initial adsorption configuration (one-side adsorption with the ether group) is shown in Fig. 3(b), where z-coordinate of the oxygen atom (O1) is set to be $z=0$. We have successively calculated the total energy as a function of the z-coordinate of oxygen. Here, two types of processes have been considered; (1) pushing down and (2) pulling up as indicated in Fig. 3(b). In each process, both the atomic positions and the unit-cell length are optimized for the given oxygen-height, and mean z-coordinate of carbon atoms, i.e., the position of the basal plane of graphene, are fixed at $z=0$. Figure 3 shows change of the total energy for the structural switching from the one-side adsorption model to the both-sides one. The results show that both the pushing down and pulling up processes result in the both-sides structure with very low activation barrier ($\sim$0.01 eV). Even for the pulling up process, the oxygen atom denoted as ”O2” in Fig. 3(b) is forced to penetrate to the other side of graphene, being followed by the formation of the both-sides structure. Since the conformation change between the structures (A) and (B) in Fig. 3(c) can easily occur, each oxygen-row acts as a flexible hinge of the folding graphene sheet. Such a capability of oxygen atoms on graphene could lead to a new manufacturing perspective like a nano-scale origami [18].

4. Summary
We have investigated the structural properties with regard to the oxygen adsorption on the graphene sheet using first-principles calculations within the density functional theory. We have found the oxygen-adsorbed graphene shows the structural bistability between the epoxy group phase and the ether one. The ether group structure is more stable than the epoxy one and prefers to form the both-sides fashion, while the one-side adsorption structure appears only as a meta-stable phase. This means the oxygen rows play a role just like a hinge of the folding screen.

Acknowledgments
We acknowledge fruitful discussions with Professor Shigeo Horiuchi. This work was partly supported by a Grant-in-Aid for Scientific Reserach from MEXT.

References
[1] S. Horiuchi, T. Gotou, M. Fujiwara, T. Asaka, T. Yokosawa, and Y. Matsui, Appl. Phys. Lett. 84, 2403 (2004).
[2] S. Horiuchi T. Gotou, M. Fujiwara, R. Sotoaka, M. Hirata, K. Kimoto, T. Asaka, T. Yokosawa, Y. Matsui, K. Watanabe, and M. Sekita, Jpn. J. Appl. Phys. 42, 1073 (2003).
[3] T. Cassagneau, F. Guérin, and J.H. Fendler, Langmuir 16, 7318 (2000).
[4] X.S. Du, M. Xiao, Y.Z. Meng, A.S. Hay, Synth. Metals 143, 129 (2004).
[5] T. Szabó, A. Szeri, I. Dékány, Carbon 43, 87 (2005).
[6] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.E. Piner, S.T. Nguyen, and R.S. Ruoff, Nature 442, 282 (2006).
[7] J.-L. Li, K.N. Kudin, M.J. McAllister, R.K. Prud’homme, I.A. Aksay, and R. Car, Phys. Rev. Lett 96, 176101 (2006).
[8] H.C. Schniepp, J.-L. Li, M.J. McAllister, H. Sai, M. Herrera-Alonso, D.H. Adamson, R.K. Prud’homme, R. Car, D.A. Saville, and I.A. Aksay, J. Phys. Chem. B 110, 8535 (2006).
[9] P.M. Ajayan and B.I. Yakobson, Nature 441, 818 (2006).
[10] A. Incze, A. Pasturel, C. Chatillon, Surf. Sci. 537, 55 (2003).
[11] A. Incze, A. Pasturel, C. Chatillon, Appl. Surf. Sci. 177, 226 (2001).
[12] M. Tsukada et al., computer code TAPP (University of Tokyo, Tokyo, Japan, 1983-2006).
[13] J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, Surf. Sci. 341, L1037 (1995).
[14] J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, Phys. Rev. B 54, 5586 (1996).
[15] W. Kohn and L.J. Sham, Phys. Rev. A 140, 1133 (1965).
[16] J.P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
[17] D. Vanderbilt, Phys. Rev. B 41, R7892 (1990).
[18] T.W. Ebbesen and H. Hiura, Adv. Mat. 7, 582 (1995).