Density Functional Study of A Photo-Induced Phase in Graphite

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Abstract. We study a novel domain with inter-layer \(\sigma\)-bonds induced by the irradiation of visible photons in graphite. The adiabatic path to nucleate this minimal domain from the starting graphite is clarified by means of the \textit{ab initio} total energy calculation. The height of the minimal barrier is shown to be 3.43eV, being just in the visible region. This domain is also shown to be sufficiently stable against the thermal fluctuation at room temperature. The electronic state of this domain has a pseudo gap, characteristic to an insulator immersed in the original semi-metallic graphite.

1. Introduction

Recently Kanasaki et al discovered a novel photo-induced phase in graphite [1]. The graphite is a layered material that each layer has a semi-metallic continuum by construction of the \(sp^2\)-bond and each of them are very weakly bounded. By the irradiation of visible lights with the energy 1.57eV, polarized perpendicular to the graphite layer, a novel nano-scale domain is induced in the graphite. The STM measurement shows a trough structure at its surface and the contraction of the inter-layer distance. By them, the \(\sigma\)-bonds are expected to be formed between graphite layers, whence the \(sp^3\)-like bonds are induced. The resultant domain includes more than 1000 carbons and is stable for more than 10 days at room temperature. We refer the new domain ‘diaphite’ hereafter.

One can easily infer that this phenomenon is closely related to the graphite-diamond conversion. The adiabatic barrier between the graphite and the diamond has been estimated to be 0.33eV/atom by Fahy et al., by means of the \textit{ab initio} total energy calculation with the local density approximation (lda) [2], but they have assumed that whole carbons uniformly transforms from the graphite to the diamond. To trigger such a transition, a macroscopic order of energy is required and the corresponding process is realized by application of a high temperature and a high pressure (3000\(^\circ\)C, 15GPa) [3].

The present phenomenon is entirely different from such a global and macroscopic phase transition. The diaphite domain is realized only through iterative local domain formation by a successive visible photon excitation and is still surrounded by the semi-metallic continuum of the original graphite. In this case, the incommensurate energy at the domain boundary surely exists and its appropriate treatment is a key theoretical issue. Hence here we have estimated the adiabatic path to nucleate the minimal diaphite from the starting graphite, by taking into account the local domain formation. In the following sections, the method and results are given.

2. Adiabatic path to the diaphite
To estimate the adiabatic path to the diaphite, we have performed the \textit{ab initio} total energy calculation with the lda. The wave function is used the LCAO form based on the gaussian STO-3G. Although the STO-3G basis may not be adequate for the structure optimization, the error coming from the cluster size is larger than that coming from the basis size in the present problem, and our main conclusion will not be changed even if the highly accurate basis is used. Our numerical implementation is basing on the gamess code \cite{4}. We have performed the calculation on a large carbon cluster with a 2 layers AB-stacking structure, consists of 294 carbons per layer, to take into account the local domain formation. We haven’t applied the periodic boundary condition (pbc) since the local deformation of the lattice breaks the translational symmetry of the system, and the cluster edge in \textit{ab}-plane has been terminated by Hydrogens. We start with the graphite structure with the intra-layer bond distance 1.42 Å and the inter-layer bond distance 3.35 Å. The local deformation of the lattice is introduced with the displacements as seen in Fig.1. Here we define the domain as the region that carbons sunk down more than $\Delta z / 2$, and the number of carbons in the domain is referred for $N_d$. The structure of the domain boundary is optimized at each domain size.

**Figure 1.** A schematic explanation of the trial deformation pattern. (a) The disk type intrusion from the graphite layer. Its amplitude is referred for $\Delta z (> 0)$. At the inside the domain, a buckling is introduced as given in (b). (b) The diaphite type buckling, inferred from the STM measurement, in which one third of carbons sink down with amplitude $\delta (> 0)$, and two thirds of carbons rise up with amplitude $\delta / 2$, in each six membered ring.

**Figure 2.** The estimated adiabatic path to the diaphite. The energy is referenced from that of the starting complete graphite. (a) The total energy versus the total intrusion $(\Delta z + \delta)$[Å]. In real process, the diaphite is realized through the photo-excitation and the lattice relaxtion process. (b) The domain size, $N_d$, dependency of the energy of the barrier top and the local minimum.

The estimated adiabatic path is given in Fig.2. The lowest barrier is given with $N_d = 26$. The top of the barrier has the energy 3.43eV and the new structure has appeared at the energy 3.30eV with the total intrusion 0.57Å $(\Delta z = 0.5, \delta = 0.07)$. Then the inter-layer distance has contracted up to
The energy at the diaphite is 0.13eV lower than that at the top of the barrier. It is sufficient to stabilize the structure against the thermal fluctuation at room temperature. Roughly speaking, the height of the barrier is twice of the energy of the irradiated light. Then it needs three or more light quanta to overtake this barrier.

The $N_d$ dependency of the barrier top and the local minimum is given in Fig.2b. The optimal domain size is determined by competition between the decrease of the incommensurate energy at the domain boundary and the increase of the deformation energy from the graphite structure as the domain becomes larger. As a result the height of the barrier takes a minimum value at $N_d = 26$.

The density of states (DOS) at the graphite and the diaphite is given in Fig.3. The graphite shows its specific semi-metallic nature around the Fermi energy. At the diaphite, the band gap doesn’t open but the value near the Fermi energy is reduced, especially peaks at about $\pm 3$eV in the graphite have disappeared in the diaphite. Then the electronic state of the diaphite has a pseudo-gap, characteristic to the insulator immersed in the original semi-metallic graphite.

![Figure 3. The DOS of the graphite and the diaphite by means of a tight-binding approximation (tba) [5], in that parameters are deduced from the lda calculations. The tba is used for an appropriate treatment of itinerant π - orbitals of the surrounding graphite. The calculation has been performed on a 2 layers AB-stacking carbon cluster, each layer contains about 2600 carbons, with the pbc. The zero of energy is the Fermi energy of each state.](image)

3. Conclusion
We have estimated the adiabatic path to nucleate the minimal diaphite. The height of the minimal barrier becomes 3.43eV, and it is able to be overtaken by few visible photons. The diaphite is sufficiently stable against the thermal fluctuation at room temperature. Although the electronic state of the diaphite has a pseudo gap, it’s still close to that of the graphite due to the itinerant π -orbital of the surrounding graphite. According to increase of the domain size through a successive photo-excitation, the $sp^3$ nature will dominate.

Here we have clarified only static nature of the diaphite. In real process, the diaphite is realized through the photo-excitation and the lattice relaxation process as schematically depicted in Fig.2a. For a deeper understanding of this photo-induced structural phase transition, then, the dynamical treatment of the process is necessary and we will discuss about it elsewhere.

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