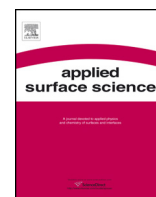




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An important atomic process in the CVD growth of graphene: Sinking and up-floating of carbon atom on copper surface



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ABSTRACT

By density functional theory (DFT) calculations, the early stages of the growth of graphene on copper (111) surface are investigated. At the very first time of graphene growth, the carbon atom sinks into subsurface. As more carbon atoms are adsorbed nearby the site, the sunken carbon atom will spontaneously form a dimer with one of the newly adsorbed carbon atoms, and the formed dimer will up-float on the top of the surface. We emphasize the role of the co-operative relaxation of the co-adsorbed carbon atoms in facilitating the sinking and up-floating of carbon atoms. In detail: when two carbon atoms are co-adsorbed, their co-operative relaxation will result in different carbon–copper interactions for the co-adsorbed carbon atoms. This difference facilitates the sinking of a single carbon atom into the subsurface. As a third carbon atom is co-adsorbed nearby, it draws the sunken carbon atom on top of the surface, forming a dimer. Co-operative relaxations of the surface involving all adsorbed carbon atoms and their copper neighbors facilitate these sinking and up-floating processes. This investigation is helpful for the deeper understanding of graphene synthesis and the choosing of optimal carbon sources or process.

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1. Introduction

Recently, the growth of graphene by chemical vapor deposition (CVD) on metal substrates [1–8] has attracted particular attentions, since it is a promising method to prepare samples at large scale composed of predominant single layer graphene and as-grown graphene can be easily transferred to other substrates [7,9–11]. Among the studied metals, copper is widely used and is recognized as the best substrate [7,12]. While, there exist several quite different recipes [5,13,14] for the preparation of large scale graphene on copper substrate and the obtained samples still display considerable imperfections. In order to choose a stable process of graphene preparation or to improve it, it is highly desirable to understand the underlying atomic details in the CVD growth of graphene on copper substrate.

With the aid of first principle calculations, many studies focusing on the configurations, energies [15–20] and nucleation kinetics [21–23] of small carbon clusters on copper surface have been reported. While, most of these studies concentrated on the

properties of carbon atoms above the top layer of copper surface, probably due to the low carbon solubility in copper; only a few of them [21,23] have involved the properties of the subsurface carbon atoms, which may also play a great role at the early stages of graphene growth since they are recently reported [21] to be more stable than that on the top of copper surface. Riikonen et al. [21] reported that carbon atoms would diffuse directly to subsurface sites only at rather moderate (0.04 ML) carbon concentrations due to a copper-layer mediated stress, and that such subsurface buried carbon atom could be dragged on the top of the surface when another carbon atom is adsorbed on a neighboring site, eventually forming a carbon dimer. When the new adsorbed carbon atom is not right above but aside the subsurface one, it needs to conquer a 0.37 eV energy barrier to drag the subsurface carbon atom up according to Wu et al.'s [23] work. Additionally, in these studies, only the most ideal situation, in which the carbon atoms were distributed completely uniformly, was considered; the co-operative relaxation of the co-adsorbed carbon atoms in facilitating the surface-to-subsurface and subsurface-to-surface migration (sinking and up-floating), which may play an important role since the carbon atoms should distribute randomly on copper surface in the real growth process of graphene, was not taken into account. So, it is very required to carry out investigations focus

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on the subsurface carbon atoms at the early stages of the growth of graphene on copper surface, taking the co-operative relaxation effect of the co-adsorbed carbon atoms into account.

In this study, we aim to clarify the details and mechanisms of the sinking and up-floating of carbon atom on the copper surface under the action of the co-operative relaxation of the co-adsorbed carbon atoms, based on density functional theory (DFT) calculations. Two carbon adsorbents are studied, corresponding to 0.12 ML (monolayer) concentration, to investigate if the co-adsorption of carbon atoms into nearby sites will facilitate the sinking of carbon atom into the subsurface sites: migration into subsurface has been suggested to encounter a significant energy barrier at 0.11 ML (1 carbon atom on 3×3 supercell) concentration [21]. Then, the mechanisms behind the sinking of carbon atom into subsurface, which dramatically depended on the co-operative relaxation effect of the two co-adsorbed carbon atoms, are discussed. Finally, we test if the sunken carbon atom could be dragged up when a new carbon atom is adsorbed aside it under the action of the collaborated effect of the third co-adsorbed carbon atom.

2. Computational details

Calculations were performed with the framework of density functional theory (DFT) using the Dmol³ implementation [24,25] in Materials Studio of Accelrys Inc. Electron exchange and correlation effects were described by the Perdew-Burker-Ernzerhof (PBE) method [26], a generalized gradient approximation (GGA)-type exchange-correlation function. Double- ζ numerical basis set with polarization functions (DNP) and DFT semicore pseudopotential (DSPP) were used. For all calculations, the real-space cutoff of plane wave was set at 4.4 Å; the k -point mesh was set to $2 \times 2 \times 1$; and no Fermi smearing was adopted. The cutoff and k -point sampling were carefully tested to produce converged results. The tolerances of energy, gradient, and displacement convergence were 1×10^{-5} hartree, 2×10^{-3} hartree/Å and 5×10^{-3} Å, respectively. And the self-consistent-field (SCF) density convergence threshold value was set at 1×10^{-6} hartree.

The copper (1 1 1) surface was modeled by a periodic 4-layer slab of 4×4 supercells. One slab contains 64 Cu atoms and the repeated slabs are separated by about 10 Å vacuum to avoid interactions between neighboring slabs. During all the calculations, the bottom two layers of copper atoms were fixed, whereas the other layers were allowed to relax. This strategy has been tested by only fixing the bottom layer, and the total energy of the system merely decreased by about 0.06 eV.

The adsorption energies E_{ads} are defined as

$$E_{\text{ads}} = -\frac{E_{\text{nc+surface}} - E_{\text{surface}} - n\mu}{n} \quad (1)$$

where $E_{\text{nc+surface}}$ stands for the total energy of the species adsorbed on the surface, E_{surface} is the energy of the clear stepped Cu (1 1 1) surface without adsorbates, and μ is the chemical potential of carbon, which is defined as the energy of an isolated carbon atom in vacuum here. The quantity n denotes the number of carbon atoms adsorbed on the surface. With this definition, the positive E_{ads} values correspond to stable (exothermic) adsorption on the surface.

3. Results and discussions

3.1. The sinking of carbon atom when two carbon atoms are co-adsorbed into nearby sites

In this section, two co-adsorbed carbon atoms are considered. All the possible arrangements of the two carbon atoms, which may affect each other, are illustrated in Fig. 1. The blue spheres labeled F and H represent FCC and HCP sites on the copper (1 1 1) surface,

Table 1
The adsorption energies per carbon atom.

Structure	E_{ads} (eV)	Structure	E_{ads} (eV)
Dimer	6.67	<i>BM1 + C3</i>	5.23
<i>BM1</i>	5.39	<i>BM2 + C2</i>	5.21
<i>BM2</i>	5.42		
BM1 + C1	6.11		
BM1 + C2	6.16		
BM2 + C1	6.13		

Italic indicates structures owning sunken carbon atom.

respectively; and the white spheres labeled t^* , b^* and h^* , correspond to some top, bridge and hollow sites, respectively. For every combination of two co-adsorbed carbon atoms, we first put one carbon atom on a blue sphere site and then another one on a white sphere.

The high carbon concentration (0.12 ML), considered in the present work, should, according to Ref. [21] effectively block carbon migration to the subsurface. While this conclusion was based on calculations employing the 3×3 supercell using the nudged-elastic band method with periodic boundary conditions, in the present work we test spontaneous migration of atoms in a larger unit cell by geometry optimization. We observe co-operative relaxations that facilitate carbon migration toward subsurface. The optimized configurations after geometry optimization are given in Fig. 2. Two types of configurations, called bridging-metal1 (BM1) and BM2 structures respectively, with one carbon atom having sunken into subsurface have been obtained, when the two arranged carbon atoms cannot evolve to the nearest neighbor hollow sites and coalesce directly without over bridge diffusions.

Structure BM1 is evolved from the initial configurations with carbon pairs arranged on sites F-t3, b3, h2, h3, h4 and H-t3, b3, b4. Structure BM2 is evolved from that with carbon pairs arranged on sites F-b4 and H-h1. For more clear description, the carbon atoms above the copper surface are colored by blue, while the subsurface ones are colored by gray. Under other circumstances, when the two carbon atoms can evolve to the nearest neighbor hollow sites with no need for over bridge diffusion (contain that exactly locate at the nearest neighbor hollow sites), such as the carbon pairs on sites F-t1, b1, h1, b2, t2 and H-t1, b1, b2, t2, they will coalesce directly and form a carbon dimer on the surface (called Dimer structure).

The difference between these two types of BM structures is the sunken carbon atom in BM1 structure stays at a position below a HCP site, namely a tetrahedral site, while in BM2 structure stays at a position below a FCC site, namely an octahedral site. In both of these BM structures, the C-Cu-C chains are almost linear in top view. While, as there exists repulsive interaction between the sunken carbon atom and the copper atom right beneath it in the BM1 structure, the linearity of the C-Cu-C chain deviates about 18.5°. The carbon atom left on the surface in the BM1 structure forms a 4-fold coordinated configurations, and the coppers in the surface lattice show large atomic displacements, which is characteristic for the bridge adsorption site [21]. For example, the shared copper atom has been pulled (pushed) upward from the surface.

The stability of these two types of BM structures is characterized by the adsorption energies per carbon atom, which are listed in Table 1. It can be seen that, the adsorption energies per carbon atom in both BM structures are very approximate, while, that in the dimer structure shows about 1.26 eV larger. This means, that the Dimer structure is much more stable than the BM structures and the stability of the both BM structures are nearly the same. Taking the forming conditions of the Dimer and BM structures into account, this difference in adsorption energies indicates that, when the surface concentration of carbon atoms is large enough for every carbon atom to coalesce directly with others, the formation of carbon species (like dimer) on the surface will be dominant and the

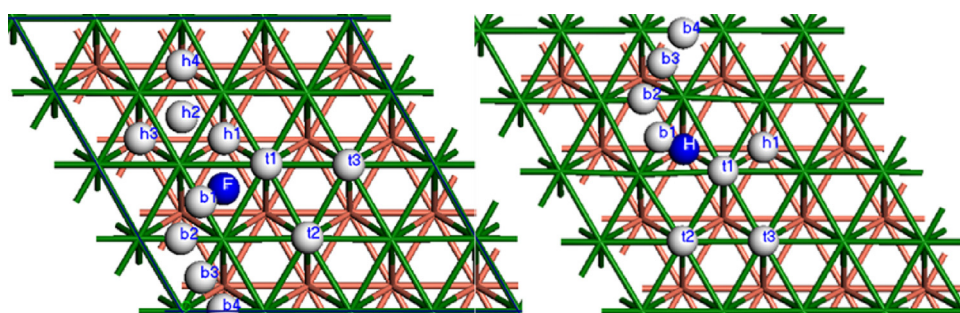


Fig. 1. Adsorption sites on the copper (111) surface. The blue spheres, labeled F and H, mean FCC and HCP adsorption sites; the white spheres, labeled t^* mean top sites, labeled b^* mean bridge sites, labeled h^* mean hollow sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

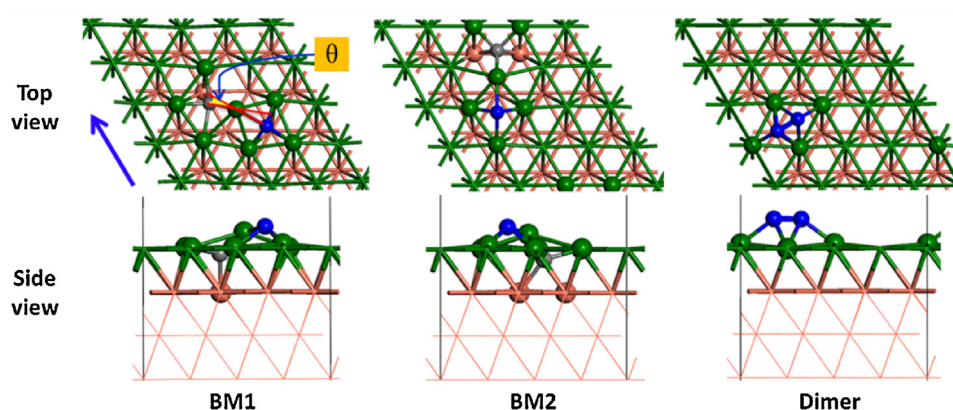


Fig. 2. The optimized configurations of two types of BM structures and one type of dimer structure obtained. Blue spheres represent carbon atoms above the surface and gray spheres represent that under the surface. Both top and side views are presented, and the side view along the orientation indicated by the blue arrow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

formed carbon species should be very stable and never decompose or sink into subsurface again.

The calculations in this section suggest that: (1) at the very first stages of the CVD synthesis of graphene on copper surface, as the surface concentration of carbon atoms is lower, they may sink into the subsurface. This is consistent to the conclusion in Ref. [21] that carbon atoms populate the subsurface site at the early stages of graphene growth. While in the present case, we suggest that this can happen at higher concentrations (0.12 ML) than those proposed in Ref. [21] (0.04 ML), due to the co-operative relaxations. (2) With the increasing of the carbon atom concentration, the sinking of carbon atom into subsurface will be effectively blocked by the formation of carbon species (like dimer) on the copper surface, since the formed carbon species is quite stable. This is different from the conclusion in Ref. [21] that the migration of carbon atom into subsurface is blocked by the copper-mediated carbon monomer repulsion.

3.2. The mechanisms behind the sinking of carbon atom into subsurface

Taking the evolution process from the arrangement of F-h3 to BM1 structure (as shown in Fig. 3) as an example, the mechanisms behind the sinking of carbon atom into subsurface are discussed. The important role of the co-operative relaxations, which causes the strengths of the C–Cu bonds between the adsorbed carbon atom and its three nearest copper atoms become unequal, has been emphasized. The strength of the C–Cu bonds is characterized by the deformation electron densities (defined as the total electron density with the density of the isolated atoms subtracted), in which the positive values indicate net electrons are remained and a C–Cu

Table 2

The distances labeled in Fig. 3f through the evolution from arrangement F-h3 to the BM1 structure.

Conf.	Distance (Å)						
	l_1	l_2	l_3	l_4	l_5	l_6	l_7
a	2.621	2.630	2.697	2.706	2.570	2.569	2.770
b	2.464	2.475	3.084	3.101	2.531	2.530	3.181
c	2.362	2.367	3.327	3.349	2.589	2.586	3.284
d	2.394	2.408	3.265	3.314	2.618	2.609	3.321
e	2.389	2.433	3.164	3.447	2.603	2.504	3.003

Length of copper bond on clear copper (111) surface: 2.556 Å.

bond is formed. The strength of the C–Cu bond is proportional to the value of the deformation electron density between corresponding carbon and copper atom. The deformation of the copper lattice caused by the adsorbed carbon atoms through this evolution process is characterized by the Cu–Cu distances, which is labeled in Fig. 3f and listed in Table 2.

The original structure in this evolution process is given in Fig. 3a. As the copper atom labeled S is shared by two carbon atoms, the equality of the C–Cu bond's strength between each carbon atom and its three nearest copper atoms is broken: the ones linking to copper atom S become weaker than those linking to copper 1, 2, 3 and 4. Then, under some arbitrary perturbations, this inequality of the C–Cu bond's strength results in that, carbon atom C1 moves toward copper atom Cu1 and Cu2 gradually and the bond strength between it and Cu1, Cu2 become stronger and stronger. At Fig. 3b, carbon atom C1 has moved into a bridge-site between copper atoms Cu1 and Cu2, pushing them apart; and at the same time, copper atom S is pulled upward by carbon atom C1. This typical deformation of the surrounding copper lattice upon carbon

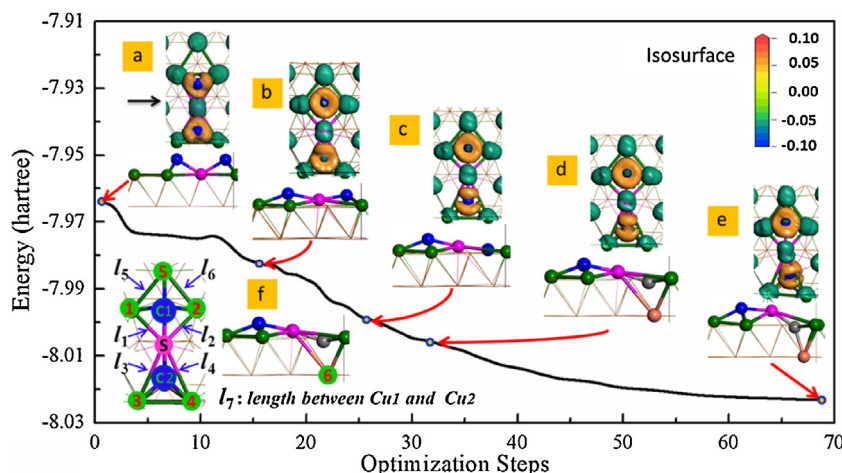


Fig. 3. The energy curve and typical configurations in the evolution process from arrangement F-h3 to the BM1 structure. The values of energy are added by 14310.0 hartree for clear. And some atoms and distances are labeled in f for convenient. The deformation electron density, which is defined as the total density with the density of the isolated atoms subtracted, is mapped to characterize the strength of the C–Cu bonds.

adsorption is characteristic for the bridge adsorption site and has earlier been discussed in Ref. [21]. As a result, the hole enclosed by copper atoms S, Cu3 and Cu4 becomes significantly larger. After the carbon atom C2 begins to migrate into the surface. Fig. 3c is the transient configuration that carbon atom C2 just migrates into the surface at a particular point of time. However, by now, since the copper atoms in the second layer begin to interact with carbon atom C2, this configuration is quite unstable and carbon atom C2 will sink into subsurface continuously. Fig. 3d shows another unstable intermediate configuration, in which copper atom Cu6 is right below carbon atom C2. Due to the repulsive interaction from copper atom Cu6, finally, carbon atom C2 slips to one side of Cu6 slightly, and stays at a position shown in Fig. 3e.

What's shown in Fig. 3 is the most basic evolution process of the surface-to-subsurface migrating of carbon atom facilitated by the co-operative relaxations of two carbon atoms. In the situations starting from the arrangements of F-h2, F-h4 and H-h1 (corresponding results are provided in Supplementary Material), the surface-to-subsurface migrating process of carbon atom becomes more complicated and can be split into two stages: the sinking of one carbon atom into subsurface, and its subsurface diffusion till arriving at the most stable sites. The mechanism behind the sinking of carbon atom is similar to that has been described above. What should be mentioned is that, the subsurface diffusion of such sunken carbon atom to its stable positions (the tetrahedral and octahedral sites in BM1 and BM2 structures, respectively) is completely spontaneous. This is quite different from the results in Ref. [21] and Ref. [27], in which the activation energy about 1.0 eV and 1.5 eV is needed respectively. This difference indicates that, the co-operative relaxation of the co-adsorbed carbon atoms can facilitate

not only the migration of carbon atom into subsurface, but also the subsurface diffusion of the sunken carbon atom.

Taking into account that the carbon concentration considered in the present case, 0.12 ML, is already greater than the value of 0.11 ML which can effectively block the migration of carbon atom into subsurface [21], it should be concluded that the co-operative relaxations of the two carbon atoms facilitate the migration of carbon toward subsurface: when two carbon atoms are co-adsorbed, the co-operative relaxation of them will result in the interactions between each carbon atom and its nearest three copper atoms become unequal, and then this inequality makes one of them sinks into subsurface. Furthermore, based on analyzing the relaxation process from arrangements F-h2, F-h4 and H-h1, we also find that the co-operative relaxation of two co-adsorbed carbon atoms can facilitate the subsurface diffusion of the sunken carbon atom.

3.3. The up-floating of the sunken carbon atom with co-adsorption

After clarifying the details and the mechanisms for the sinking of carbon atom into subsurface, we divert our attentions to study whether these sunken carbon atoms can up-float again when another carbon atom is co-adsorbed aside it under the action of the co-operative relaxation of the third co-adsorbed carbon atom. The adsorption sites tested, for the BM1 and BM2 structures, are illustrated in Fig. 4a and b respectively. To distinguish them from their position relative to the C–Cu–C chain in the BM structures, sites 1 and 2 in Fig. 4a and site 1 in Fig. 4b are named “side” sites, while, sites 3 in Fig. 4a and site 2 in Fig. 4b are named “counter” sites.

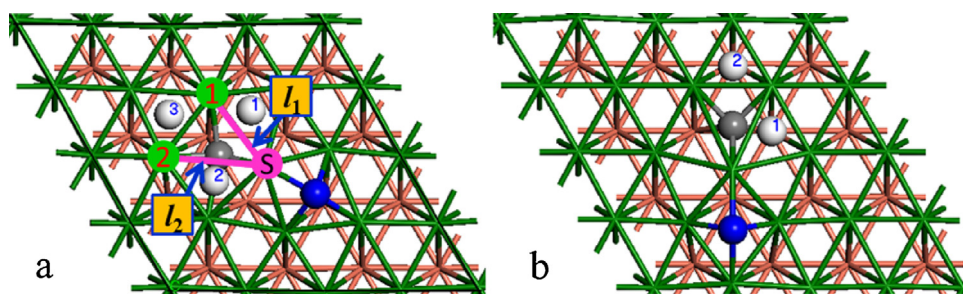


Fig. 4. The sites designed for the imported carbon atoms in the attempts to drag the sunken carbon atom up. The symbols in “a” are used to simplify the descriptions.

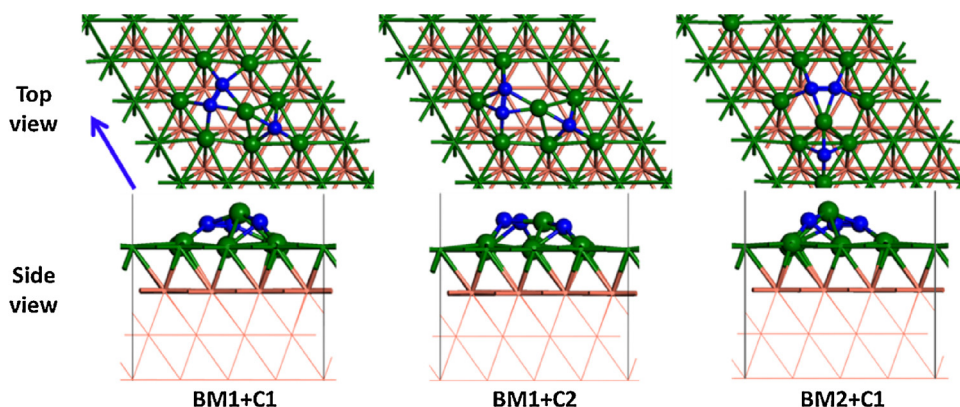


Fig. 5. The final configurations when the imported carbon atom is put at the “side” sites around the sunken carbon atom.

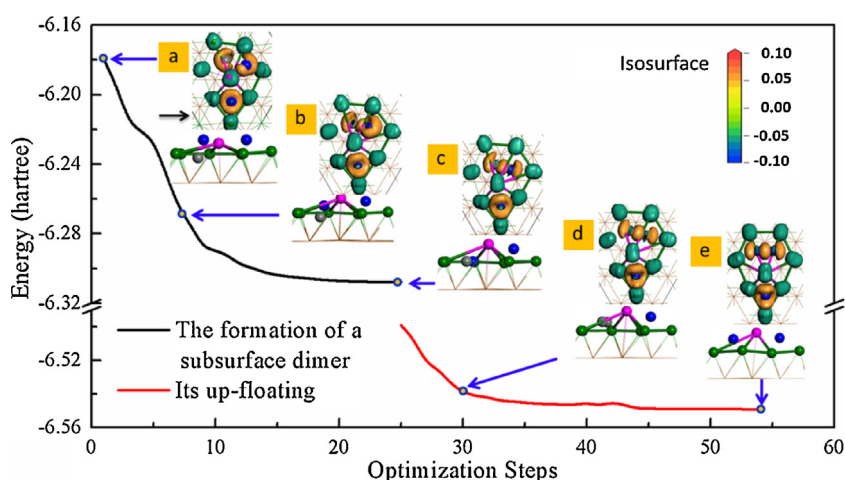


Fig. 6. The energy curve and typical configurations in the evolution process of the system in which one carbon atom is put on the site 1 in the BM1 structure. The values of energy are added by 14350.0 hartree for clear. The deformation electron densities are mapped to characterize the bonding situations.

Fig. 5 shows the successful results in dragging the sunken carbon atom up after geometry optimizations. It can be noted that, all of these three configurations are evolved from the arrangements in which the new co-adsorbed carbon atom is putted at the “side” sites around the sunken one. These results indicate that the collaborated effect of the third co-adsorbed carbon atom, which is left on the surface in the BM structure, plays an important role in facilitating the up-floating of the sunken carbon atom, since it has been proposed [21] that the subsurface buried carbon atom can only be dragged up when the new imported carbon atom is right above the sunken one. Another phenomenon should be noted is that, the two carbon atoms in the formed dimer can stay at two neighbor bridge sites (BM1 + C1 and BM2 + C1) or two neighbor hollow sites (BM1 + C2), and their adsorption energies are nearly the same.

The up-floating processes of the sunken carbon atom in these three attempts are nearly the same, and could be divided into two steps: the formation of a carbon dimer under the topmost copper layer and its expulsion on the top of the surface. Taking the configuration evolutions process of the system in which one carbon atom is put on the site 1 in the BM1 structure as example, as shown in Fig. 6, the reason for the success of these attempts is analyzed. Even before a new carbon atom is imported, the copper-copper bond lengths l_1 and l_2 (as shown in Table 2) are already greater than the one on the clear copper surface. When the new carbon atom is imported, the interaction between the two copper atoms bonded by l_1 should be further weakened as it will be partially substituted by two pairs of C–Cu interactions (as shown in Fig. 6a). As a consequence, the bonding of the sunken carbon atom and the new adsorbed one should

be quite easy, and a subsurface carbon dimer is formed (Fig. 6b and c). While, since a dimer is only stable on top of the copper surface [27] due to the repulsive interactions from the copper lattice, the formed dimer up-floats on the copper surface finally (Fig. 6d and e). The up-floating of the sunken carbon atom is a completely spontaneous process. The fact that the formed dimer on the surface can stably locate at two sets of sites is mainly attributed to that the formation of C–C bond makes the interactions between the carbon atoms in the dimer and the copper surface significantly weaker.

Other two attempts by arranging the imported carbon atom on the “counter” sites are failing in dragging the sunken carbon atom up (their final configurations are given in Fig. 7). Taking the attempt of BM1 + C3 for example, these failures can be understood with a few simple arguments: firstly, before carbon atom C3 is imported, the bond length between copper 1 and 2 is much shorter than that between copper 1 and S; secondly, even when C3 is imported, both the copper atoms 1 and 2 are only shared by two carbon atoms, and the interaction between copper atoms 1 and 2 is still strong enough to prevent the bonding of carbon atom C3 with the sunken carbon atom. In these attempts, the imported carbon atom forms a 4-fold coordinated configuration with its nearest copper atoms finally.

As a summary, the sunken carbon atom can up-float again if another carbon atom is co-adsorbed aside it, but the success of this up-floating requires: the new co-adsorbed carbon atom must share two copper atoms with the sunken one, and at least one of these shared copper atoms should be shared simultaneously by another carbon atom, which is left on the surface in the BM structure. The up-floating process of the sunken carbon atom contains two steps:

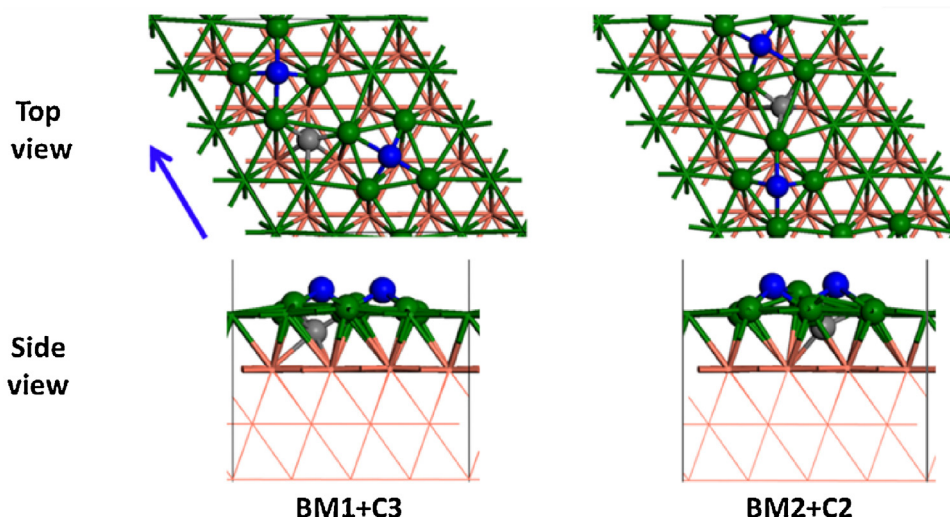


Fig. 7. The final configurations when the imported carbon atom is put at the “counter” sites around the sunken carbon atom.

the formation of a subsurface carbon dimer and its coming up. And the collaborated effect of the on-surface carbon atom plays a pivotal role in improving the formation of the subsurface carbon dimer from the sunken carbon atom and new imported one. Furthermore, from the fact that the adsorption energy per carbon atom in the successful situations (Fig. 5) shows about 0.9 eV greater than that in the failing situations (Fig. 7), it can be deduced that the up-floated carbon atom becomes more stable and is almost impossible to sink into subsurface again.

4. Conclusions

Graphene synthesis on copper surface was carefully investigated with the aid of DFT calculations. Taking the co-operative relaxation of two or more carbon atoms into account, an important atomic process at the early stages of the CVD growth of graphene on copper surface is summarized: (1) the carbon atom sinks into subsurface. As more carbon atoms are adsorbed nearby, (2) it will spontaneously form a dimer with one of the new adsorbed carbon atoms, and the formed dimer will up-float on top of the surface, subsequently. This is consistent with earlier DFT calculations [21].

The co-operative relaxation of the co-adsorbed carbon atoms plays an important role in facilitating both the sinking and up-floating of carbon atoms on the copper surface: when two carbon atoms are co-adsorbed, their co-operative relaxation will lead that the three carbon–copper interactions between one carbon atom and its nearest three copper atoms become unequal, and this inequality subsequently makes one carbon atom to sink into subsurface; when another new carbon atom is co-adsorbed aside the sunken one, the co-adsorbed effect of the carbon atom left on the surface (one of the two originally co-adsorbed atoms in the BM structures) play a pivotal role, in improving the formation of a dimer from the sunken carbon atom and new adsorbed one.

Due to this co-operative relaxation effect of the co-adsorbed carbon atoms, the conditions permitting the occurrence of the sinking and the up-floating phenomena of carbon atom are enhanced: the sinking of the carbon atom can occur at a higher (0.12 ML) carbon concentration compared with that suggested in reference [21], 0.04 ML; and the up-floating of the sunken carbon atom can take place when another carbon is co-adsorbed aside it. Similarly due to this co-operative relaxation effect, the sunken subsurface carbon atom can stably locate at not only an octahedral site [21] but also a tetrahedral site. The up-floated carbon atom gains in stability as it forms a dimer, excluding its migration back to subsurface.

This investigation provides a comprehensive microscopic picture for the atomic process at the early stages of graphene growth, and is helpful for the deeper understanding of graphene synthesis and the choosing of optimal process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2013.07.081>.

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