

The over-step coalescence of carbon atoms on copper surface in the CVD growth of graphene: density functional calculations

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The ways in which carbon atoms coalesce over the steps on copper (111) surface are ascertained by density functional theory (DFT) calculations in the context of chemical vapor deposition (CVD) growth of graphene. Two strategies, (1) by putting carbon atoms on and under the steps separately and (2) by importing additional carbon atoms between the ones separated by the steps, have been attempted to investigate if an over-step coalescence of carbon atoms could take place. Based on analyses about the optimized configurations and adsorption energies of carbon atoms nearby the steps, as well as the energy evolution curve of the system throughout the geometry optimizations process, we determined the main way in which graphene grows over the steps continuously: the carbon atoms, adsorbed additionally on the locations between the already existing ones which are separated by the steps, link them (these carbon atoms separated by the steps) together. The direct over-step coalescence of the carbon atoms separated by the steps is very difficult, although the energy barrier preventing their coalescence can be weakened by importing carbon atoms on and under the steps gradually. Our results imply potential applications in directing the fabrication of graphene with particular structure by controlling the surface topography of copper substrate. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4808202>]

I. INTRODUCTION

Due to remarkable electronic, optical and mechanical properties,¹⁻⁴ graphene shows huge potential of applications in electronic, spintronic, sensor and mechanical devices. Therefore, numerous fundamental and technological researches⁵⁻¹⁶ have been carried out since its first isolation.¹⁷ Among many techniques of graphene synthesis, chemical vapor deposition (CVD) techniques offer a promising avenue and have begun to dominate the field in recent years,⁸ especially for the case of using copper as the substrate material.⁷ Using this technique, some high-quality graphenes have been prepared with several different recipes.¹⁸⁻²⁰

In the case of graphene CVD synthesis on Cu substrate, it turns out that the sample quality is quite sensitive to various experimental conditions like temperature, carbon sources,^{13,21,22} hydrogen concentration²³⁻²⁵ and some others.²⁶⁻²⁸ But what's pleasantly surprising is that the growth of

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macroscopic pristine graphene is not limited by the underlying copper structure.²⁸ The crucial information that leads to our investigation comes from the work of Haider *et al.*²⁹ in which, by scanning tunneling microscopy, they revealed that the atomic arrangement of graphene was not affected by the morphology and atomic arrangement of copper substrate. This characteristic is very attractive and it implies practical value for the mass production of high quality graphene on rough copper substrate. However, what puzzles us is how the carbon atoms coalesce over the steps in graphene CVD growth process. A further understanding of this characteristic has potential applications in controlling the quality or fine structure of as-grown graphene.

The purpose of this work is to provide a comprehensive atomic picture for the over-step coalescence of carbon atoms on copper surface. A copper (111) surface with a monoatomic terrace and two types of steps (labeled step type1 and step type2) was constructed. And the investigations are carried out based on the geometry optimizations calculations, on the systems with carbon atoms arranged deliberately nearby the steps. This investigation gives many insights into the growth of graphene on stepped copper surface.

II. COMPUTATIONAL DETAILS

Calculations were performed with the framework of density functional theory (DFT) using the Dmol³ implementation,^{30,31} which is accurate to predict materials properties both reliably and quickly, integrated in Materials Studio of Accelrys Inc. A general description of DFT can be found elsewhere.³² What's unique in Dmol³ is that, it uses linear combination of numerical atomic orbitals for the basis set.

$$\psi_i = \sum_{\alpha} \sum_j c_{ij}^{\alpha} \varphi_j^{\alpha}(r_{\alpha}) \quad (1)$$

Where, ψ_i corresponds to one basis function, c_{ij}^{α} is the linear combination coefficient and $\varphi_j^{\alpha}(r_{\alpha})$ is the atomic orbital given numerically as values on an atomic-centered spherical-polar mesh, rather than as analytical functions.

$$\varphi_j^{\alpha}(r_{\alpha}) = \sum_{lm} R_{nl}^{\alpha}(r) Y_{lm}(\vartheta, \phi) \quad (2)$$

The radial portion $R_{nl}^{\alpha}(r)$ is obtained by solving the atomic DFT equations numerically, and the angular portion of each atomic orbital is the appropriate spherical harmonic $Y_{lm}(\vartheta, \phi)$.

Double- ζ numerical basis set with polarization d-function (DND) were used, and the real-space cutoff was set at 4.4 Å. Double- ζ numerical basis set means two numerical atomic orbital functions are used to describe each occupied atomic orbital, and polarization d-function means these atomic orbital functions include a polarization d-function on all non-hydrogen atoms.

The core electrons bounded tightly by the nuclei were treated by a Density functional Semi-core Pseudopotential (DSPP), which is generated by fitting all-electron relativistic DFT results and specifically designed to produce accurate calculations. The electron exchange and correlation effects were described by the generalized gradient approximation (GGA) in the Perdew-Burker-Ernzerhof (PBE) form.³³ The k-point mesh was set to fine level ($2 \times 1 \times 1$), and no Fermi smearing was adopted. The tolerances of energy, gradient, and displacement convergence were set to 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 stepped copper (111) surface was modeled by a periodic 4-layer slab of 4×5 supercells, and the adjacent terraces were separated by monoatomic (11-1) and (001) steps, labeled step type1 and step type2 in Figure 1(a). One slab contains 72 copper atoms and the repeated slabs are separated by about 10 Å vacuum to avoid interactions between neighboring slabs. Correspondingly, Figure 1(b) gives the STM topography of a real copper surface with steps, on which continuous graphene had been obtained. During the investigations about the coalescence of carbon atoms on this model, the bottom two layers of copper atoms were fixed, whereas the other layers were allowed

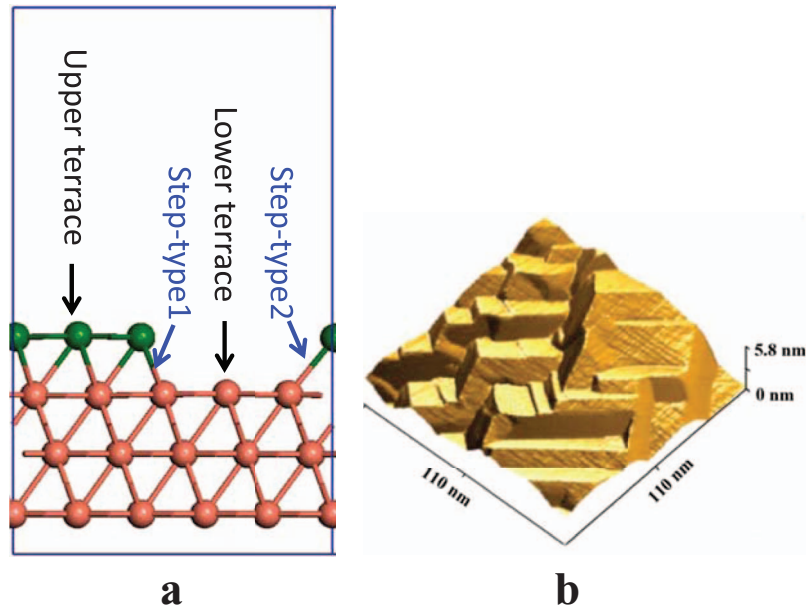


FIG. 1. (a) Side view of Cu (111) surface separated to terraces by monatomic (11-1) steps; (b) The STM topography of a real copper surface with steps.²⁹ Reprinted (adapted) with permission from Nano Lett. 11, 251 (2011). Copyright (2013) American Chemical Society.

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

$$E_{\text{ads}} = -\frac{E_{\text{nc+surface}} - E_{\text{surface}} - n\mu}{n} \quad (3)$$

Where $E_{\text{nc+surface}}$ stands for the total energy of the carbon atoms adsorbed on the surface, E_{surface} is the energy of the clear stepped Cu (111) surface without adsorbents, 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 negative E_{ads} values correspond to stable (exothermic) adsorption on the surface.

III. RESULTS AND DISCUSSIONS

In the present work, the investigations to clarify the way in which carbon atoms coalesce over the steps on copper (111) surface, are carried out based on geometry optimization calculations. At the start point, the basic properties of a single carbon atom adsorbed nearby the steps, which can provide us the foundations for the subsequent researches, are studied. Then, we turn to the central issue of this paper—to understand how the carbon atoms coalesce over the steps. Firstly, attempts by arranging carbon atoms on and under the steps separately, to see if they can coalesce together, are carried out. Secondly, additional carbon atoms are imported between the ones separated by the steps try to link them together.

In our calculation, the carbon atoms will be arranged deliberately nearby the steps, according to the purpose being concerned. All the possible adsorption sites used in subsequent calculations are labeled by white spheres with Arabic numerals in Figure 2, which corresponds to the energy minimized configurations for a clean stepped copper (111) surface.

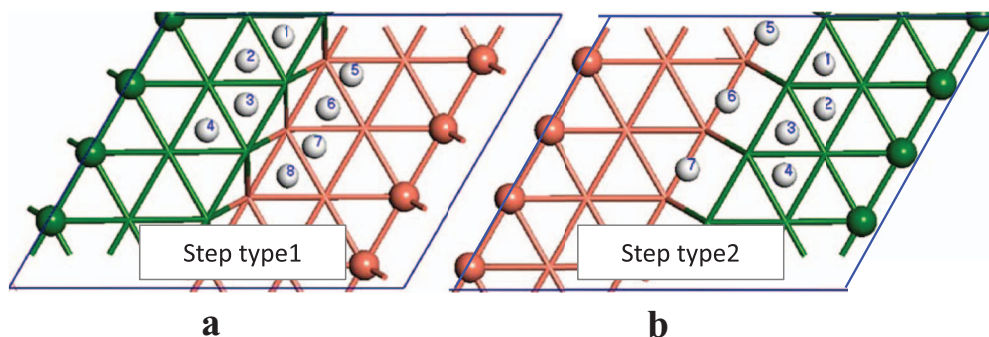


FIG. 2. The adsorption sites have been used during the calculations around (a) step type1, and (b) step type2.

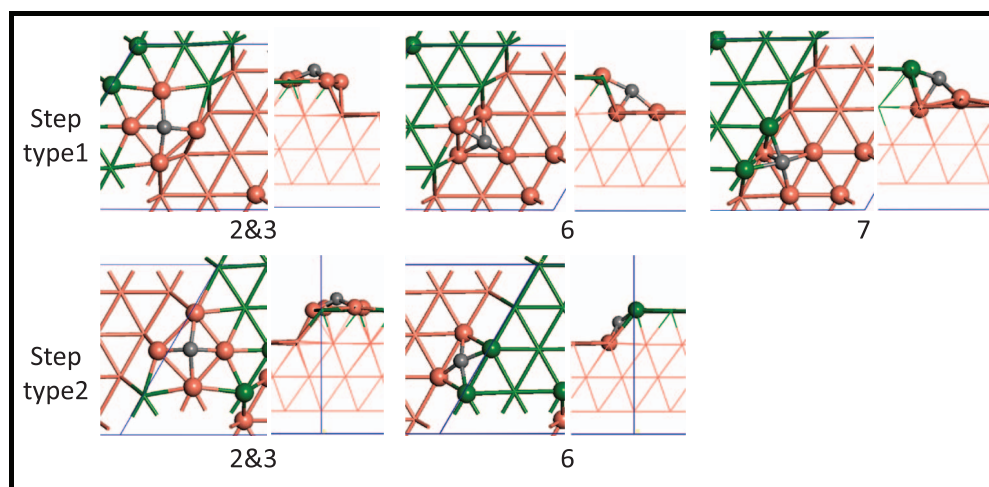


FIG. 3. The optimized configurations with single carbon atom on stepped copper surface. They are symbolized by the step types and adsorption sites at the same time. Both the top (left) and side views (right) are presented.

A. The basic properties of a single carbon atom adsorbed nearby the steps

In this section, all the seven possible adsorption sites for a single carbon atom nearby the steps, namely 2, 3, 6, 7 nearby step type1, and 2, 3, 6 nearby step type2, were tested. The energy minimized configurations and the adsorption energies per carbon atom, of these arrangements after geometry optimizations, are given in Figure 3 and Table I respectively. For comparison, the stable adsorption sites of a single carbon atom on the flat copper (111) surface were also studied (relevant results were shown in the supplementary material).³⁴

Firstly, only five sites nearby the steps on copper (111) surface were stable for the adsorption of a single carbon atom, and these sites can be roughly classified into two broad categories: (1) the adsorption sites on the upper terrace, as shown in configurations step-type1-2&3 and step-type2-2&3, and (2) the ones right above the steps, as shown in configurations step-type1-6, 7 and step-type2-6. The carbon atom adsorbed on the sites belonging to category (1) has pushed one upper-step (the junction between the upper terrace and the steps) copper atom toward the “valley”, sunk into the surface lattice, and formed a 4-fold-coordinated configuration with its nearest four copper atoms. The one adsorbed on the sites of category (2) has formed 4~5 stable C–Cu bonds with some upper-terrace and lower-terrace copper atoms, and caused slight structural reconstructions in the copper lattice.

Then, it can be observed from Table I that the adsorption energy of carbon atom adsorbed on these five sites shows about 1.0 eV higher than that adsorbed on a flat copper surface. From the point of view of thermodynamics in the gas adsorption on solid surface, this indicates that the carbon

TABLE I. Adsorption energies per carbon atom defined by equation (3).

	Step type	Conf.	(eV)	
1C on flat Cu surface ^a		FCC	5.17	
		HCP	5.13	
1C	Step type1	2&3	6.12	
		6	5.91	
		7	6.18	
	Step type2	2&3	6.06	
		6	6.48	
2C	Step type1	61	5.79	
		62	5.58	
		71&72	6.07	
	Step type2	73	5.87	
		61	6.09	
		62	6.01	
		63	5.91	
		Step type1	125	6.73
			135	6.77
561	6.51			
3C	Step type2	571	5.85	
		125	6.61	
		135	6.72	
	Step type1	561	5.67	
		1235	6.64	
		2347	6.70	
4C	Step type2	5671&6783	6.65	
		1235	6.61	
		2346	6.62	
	Step type1	5673	6.59	
		1356	6.34	
		12357	6.39	
5C	Step type2	13567	6.77	
		12356	6.33	
6C	Step type1	123567	6.66	

^aThe adsorption energies of a single carbon atom on flat copper surface is consistent with the value 4.94 eV obtained by Ping Wu³⁵ and 5.04 eV calculated by S. Riikonen.³⁶

atoms will prefer to be adsorbed on the sites near the steps rather than on the flat regions, during the growth of graphene on copper substrate, namely, the carbon nucleation should be very likely to start from the stepped regions.

Finally, the adsorption energies per carbon atom adsorbed on these five stable sites present slight differences in a range from 5.9 eV to 6.5 eV, and obey the sequence: E_{ads} (step-type2-6) < E_{ads} (step-type1-7) < E_{ads} (step-type1-2&3) < E_{ads} (step-type2-2&3) < E_{ads} (step-type1-6). We attribute this sequencing to a comprehensive effect of three arguments. The first argument is that, the C–Cu bonds linking to the upper-step and lower-step (the junction between the lower terrace and the steps) copper atoms, as shown in Figure 2, should have the biggest and smallest strength, respectively, since these copper atoms have the least and most coordinated atoms. The second one is the adsorption energy per carbon atom should be proportional to the number of C–Cu bonds that has formed, and the third one is that significant structural reconstruction of the copper lattice should result in the decrease of the adsorption energy per carbon atom, as the energy minimized configuration of a clean copper surface shows no structural reconstruction.

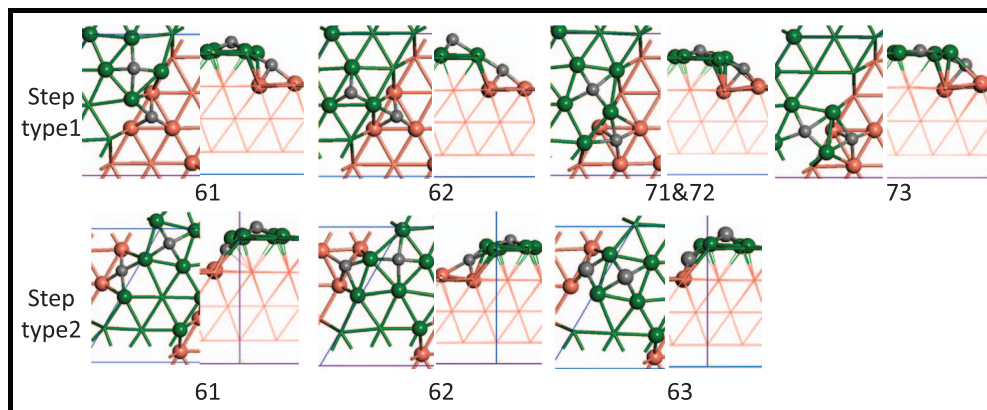


FIG. 4. The optimized configurations with two carbon atom adsorbed on stepped copper surface. Both the top (left) and side views (right) are presented.

B. Arrange carbon atoms on and under the steps separately to see if they can coalesce

Having understood the basic properties of a single carbon atom adsorbed nearby the steps, we now turn to the central purpose of this paper—to ascertain how the carbon atoms coalesce over the steps. In this section, attempts by arranging carbon atoms on and under the steps separately are carried out.

1. Two carbon atoms are arranged separately on and under the step

The arranged combinations of carbon atoms contain 6-1, 6-2, 7-1, 7-2 and 7-3 on step type1, and 6-1, 6-2 and 6-3 on step type2, which cover all the possibilities that may result to over-step coalescence. After geometry optimizations, seven stable configurations were obtained as given in Figure 4, and corresponding adsorption energies per carbon atom are also listed in Table I.

Clearly, no successful over-step coalescence of such arranged carbon atom combinations has occurred in all these arrangements. However, the adsorption energies per carbon atom under these arrangements show slight decrease (about 0.25 eV) compared with that of a single carbon atom adsorbed, which can be mainly attributed to the fact that at least one upper-step copper atom is shared by the carbon pairs in all these arrangements. Encouragingly, this indicates that the strength of the C–Cu bond linked to the upper-step copper atoms could be weakened and the coalescing barrier between two separated carbon atoms by the steps could be decreased, if these copper atoms are shared by more than one carbon atoms.

2. Import more carbon atoms to promote their over-step coalescence

Based on above analyses, further efforts have been carried out by gradually importing more carbon atoms, under the rule that these imported carbon atoms must share at least one upper-step copper atom which has already been shared by the existing carbon atoms. The designs here contain the combinations of **3C**: 125, 135, 561, 571; **4C**: 1235, 5671, 2347, 6783; **5C**: 12357, 13567; **6C**: 123567 on step type1 and **3C**: 125, 135, 561; **4C**: 1235, 1356, 2346, 5673; **5C**: 12356 on step type2.

As expected, a successful over-step coalescence of the carbon atoms has occurred in the arrangement of carbon combination 5673 on step type2. The energy evolution curves of this system are shown in Figure 5, and simultaneously five key configurations are given out. It can be seen that the over-step coalescence of carbon atoms 6 and 3 in this arrangement is a completely spontaneous process, as the energy evolution curve descends monotonically throughout all the geometry optimization steps. The success in this attempt can be attributed to the fact that the energy barrier preventing the bonding of carbon 6 and 3 is expected to reduce significantly as the two upper-step copper atoms between them are both shared by three carbon atoms. Under the perturbations introduced by the $<0.3\text{\AA}$ displacements of atoms between successive optimization steps, the carbon atoms on site 6

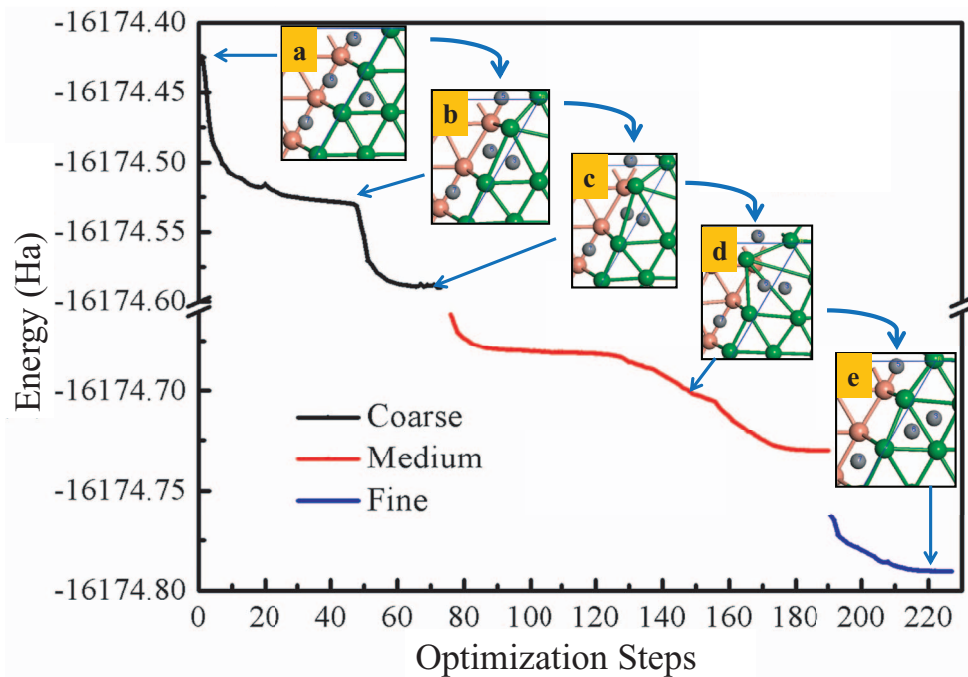


FIG. 5. The energy evolution curves and corresponding key configurations of the system with carbon atoms arranged on 5673 sites on step type 2. The black, red and blue solid lines stand for the energy evolution under coarse, medium and fine level, respectively. (a) Initial structure. (b) Just before the coalescence of carbon atoms 63. (c) Carbon atoms 63 have coalesced but the dimer generated is under the upper terrace. (d) The sunken carbon dimer came-up to a position in the upper terrace lattice. (e) The dimer is separated out.

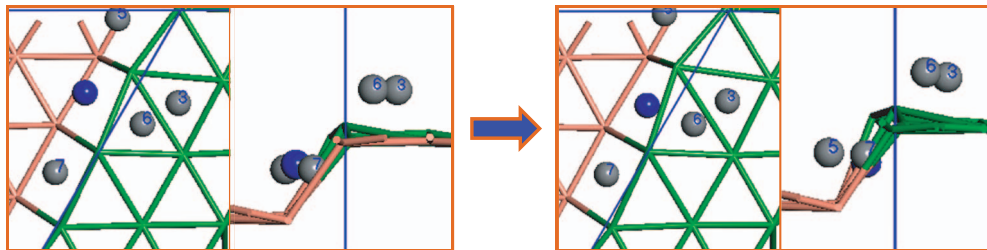


FIG. 6. The initial and final configurations when another carbon atom is put on site 6 again based on the structure of Figure 5(e).

and 3 in (a) the initial configuration (b) move together and (c) coalesce gradually forming a carbon dimer under the upper terrace, then (d) it comes-up to a position in the upper terrace lattice, and finally (e) it is separated out on the upper terrace.

This specious success demonstrates that an over-step bonding of the carbon atoms during the CVD growth of graphene is possible. Unfortunately, this process is unrepeatable when another carbon atom is put on site 6 again based on the structure of Figure 5(e). The initial and final configurations of this test are supplied in Figure 6. The reason of this non-repeatability is shown below: the formation of carbon dimer results in the decrease of the interactions between its carbon atoms and the upper-step copper atoms; this decrease then leads the distance from the carbon dimer to the upper terrace becomes larger, which results the bonding barrier between the new added carbon atom and this formed carbon dimer becomes greater. As a consequence, the new added carbon atom is more stable in its initial position than moving up to bond with the dimer.

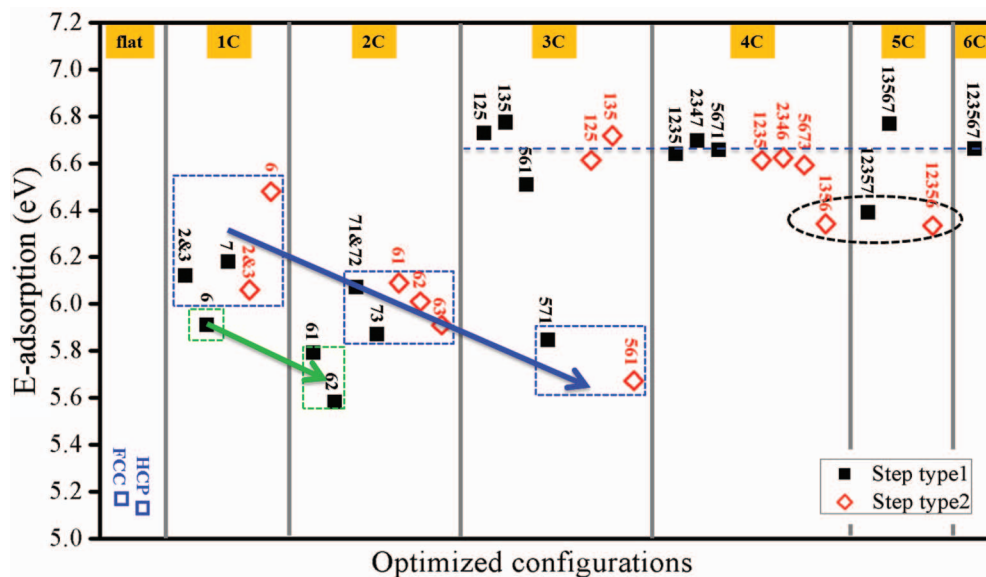


FIG. 7. Adsorption energies per carbon atom for all configurations arranged. The blue hollow squares represent the adsorption energies on flat Cu (111) surface, the black solid squares correspond to the ones on step type1, and the red hollow diamonds correspond to that on step type2. Arrangements with different number of carbon atoms adsorbed are separated by gray lines. The points, framed up by blue and green dash squares, correspond to the adsorption energies in the situations with no carbon bonds formed. Specially, the ones framed up by green squares represent the adsorption energies per carbon atoms in the configurations containing one carbon atom, which is adsorbed on site 6 and bonded with only one upper-step copper atom. The points in a black dash ellipse correspond to the adsorption energies per carbon atoms in the configurations have less number of C–C bonds, compared with those have the same number of carbon atoms.

However, all of other attempts are failing. The adsorption energies per carbon atom are listed in Table I and plotted on a scatter diagram in Figure 7. Limited by space, the energy minimized configurations of these arrangements are put in the supplementary material.³⁴

In Figure 7, it can be seen clearly that, when no carbon dimer or trimer has been formed (the data points framed up by light-blue and green-dash squares), the adsorption energies would decrease gradually with the increase in the number of carbon atoms. This is because, in these situations (step-type1-571 and step-type2-561), there exists one upper-step copper atom being shared simultaneously by the three co-adsorbed carbon atoms, which makes the coordinated number of this copper atom increases and the interactions between it and the carbon atoms are weakened. This phenomenon confirmed the deduction in III B 1 that, the coalescing barrier between two carbon atoms separated by the steps could be decreased by importing more carbon atoms.

When carbon dimer or trimer has been formed, the formation of carbon bond(s) brings significant increase in the adsorption energy of about 0.9 eV. This indicates the strength of C–C bond should be much stronger than C–Cu bonds, and implies that a newly added carbon atom prefers to be adsorbed on the sites where carbon atoms already exist. Additionally, no obvious changes in adsorption energies have been caused by importing more carbon atoms when the number of carbon atoms gets greater than three. This is because the formation of C–C chain (more than two carbon atoms) weakens not only the interactions between its carbon atoms and the copper surface, but also the C–C bond strength compared that in carbon dimer. The scatter points framed up by black dash ellipse in Figure 7 correspond to the adsorption energies per carbon atoms in the configurations which have less number of C–C bonds compared with those have the same number of carbon atoms.

The results in this section show that the direct over-step coalescence of carbon atoms is very difficult, although the energy barrier preventing their coalescence can be weakened by increasing the number of carbon atoms on/under the steps gradually. Even if such over-step coalescence can happen successfully in some special case, the formed carbon dimer is still not stable to locate at the

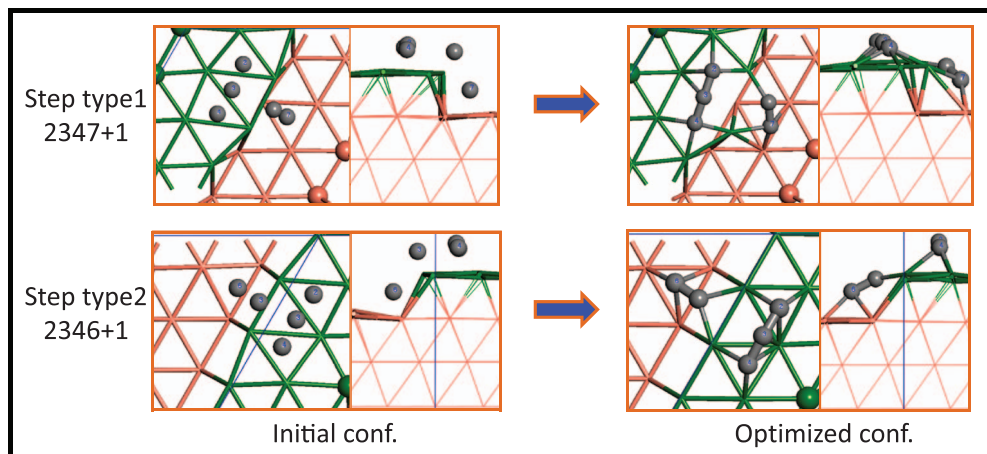


FIG. 8. The initial and optimized configurations for the arrangements with one additional carbon atom imported in the optimized configurations step-type1-2347 and step-type2-2346.

position over the step but moves to a position on the upper terrace finally. Furthermore, this kind of direct over-step coalescence becomes unrepeatably when a dimer has formed on the upper terrace.

C. Import carbon atoms between the ones separated by the steps to link them together

As the direct over-step coalescence of carbon atoms is very difficult, in this section a different strategy is adopted by importing additional carbon atoms between the existing ones separated by the steps. Some attempts based on the energy minimized configurations of step-type1-2347 and step-type2-2346 (given in the supplementary material)³⁴ are carried out.

Firstly, one additional carbon atom is imported. The initial and optimized configurations are given in Figure 8. Despite no successful over-step carbon coalescence has occurred on both types of steps in these attempts, it is still gratifying since the obtained configurations show a positive trend to a successful over-step coalescence of carbon atoms. The additional carbon atom imported has formed a dimer with the carbon atom on the lower terrace, and the formed dimers in both situations are approximately vertical to the step edges. This adsorption feature of the additional carbon atoms imported shortens the distance between the carbons separated by the steps, and makes the over-step coalescence of carbon atoms easier when some other additional carbon atoms are imported.

Then, based on above analyses, one more carbon atom is imported again in the optimized configurations as shown in Figure 8, in order to link the carbon atoms separated by the steps together. The initial and optimized configurations of these attempts are given in Figure 9. As expected, the new added carbon atom has linked the carbon atoms separated by the steps together, and a cambered carbon chain over the step has been formed. Additionally, the coalescence processes in these two attempts are completely spontaneous, since the energy evolution curves of these two systems descend monotonically throughout the geometry optimization steps (given in the supplementary material).³⁴

The probability of such kind of over-step coalescence of carbon atoms in the graphene CVD growth on copper surface is analyzed based on the adsorption energies of the fifth and sixth adsorbed carbon atoms as given in Figure 10. They are about 7.5 eV and 5.5 eV, respectively, and even the smaller value is still significantly greater than the adsorption energy per carbon atom adsorbed on a flat surface. As the adsorption probability is exponentially proportional to the value of corresponding adsorption energies, this indicates that such kind of over-step coalescence of carbon atoms should be a prone event that occurs commonly in the CVD growth of graphene. The big values of the adsorption energies for the fifth carbon atom can be mainly attribute to that it has formed a C–C bond with an isolated carbon atom. On the other hand, the obvious decrease in the values for the sixth one can be attributed to the argument that, the formation of two C–C bonds from it to the exited carbon atoms makes the strength of them weakens significantly.

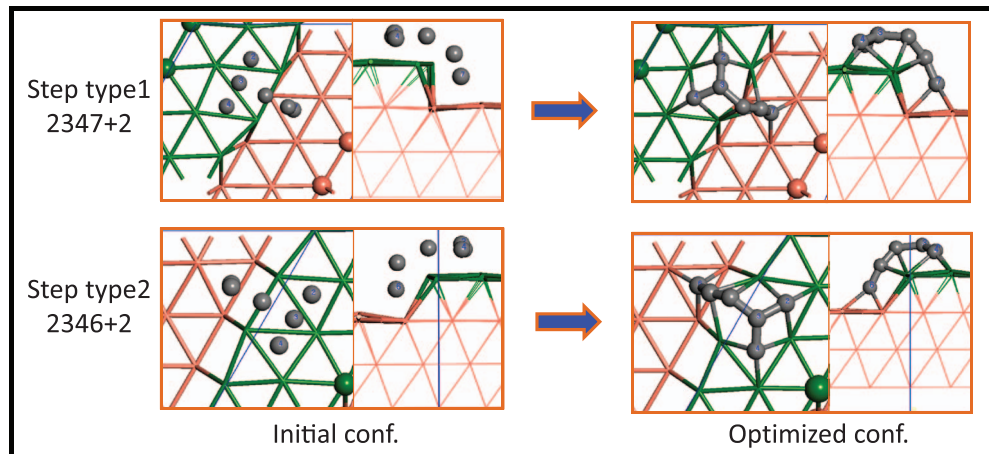


FIG. 9. The initial and optimized configurations for the arrangements with one more carbon atom imported in the optimized configurations in Figure 8.

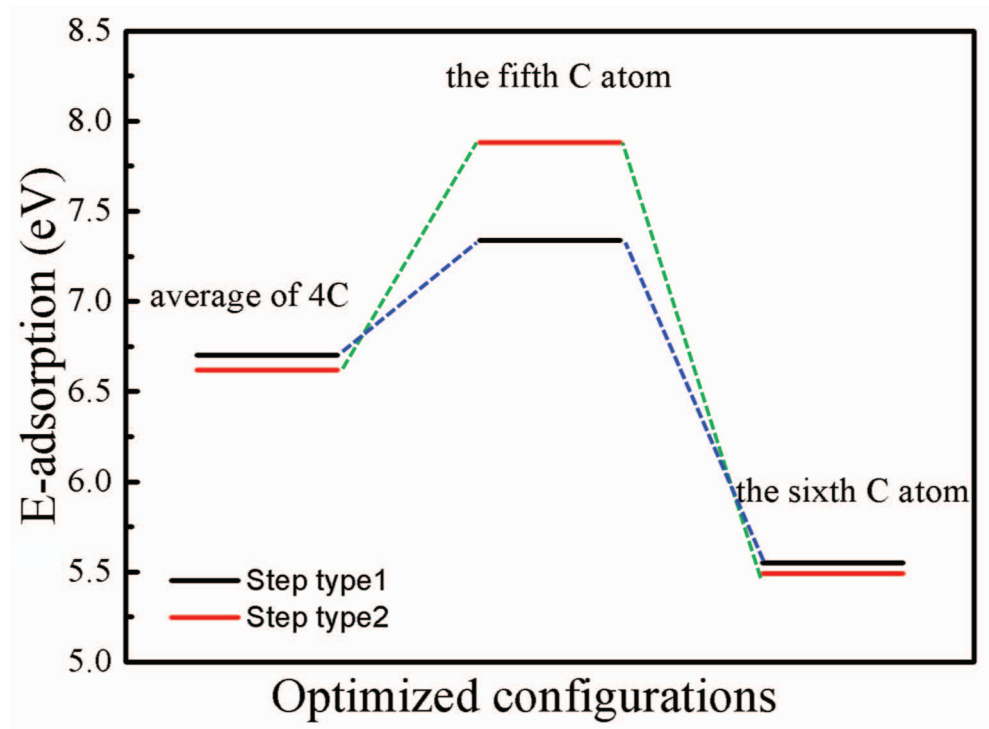


FIG. 10. The adsorption energies for the fifth and sixth carbon atoms imported.

IV. CONCLUSIONS

In this work, two strategies, (1) by putting carbon atoms on and under the steps separately and (2) by importing additional carbon atoms between the ones separated by the steps, are attempted to investigate the ways in which carbon atoms coalesce over the steps on copper (111) surface.

Based on careful configuration and energy analyses, it can be concluded that, the main way in which graphene grows over the steps is that the carbon atoms adsorbed additionally on the locations between the already existing ones, which are separated by the steps, link them (these carbon atoms separated by the steps) together. Such kind of over-step coalescence of the carbon atoms is a completely spontaneous process, and the adsorption energy about 5.5 eV for the additional

adsorbed carbon atoms implies it should be a prone event that occurs commonly in the CVD growth of graphene. The direct over-step coalescence of carbon atoms is very difficult, although the energy barrier preventing their coalescence can be weakened by increasing the number of carbon atoms on/under the steps gradually.

This knowledge gives us an insight into the atomic processes for the continuous CVD growth of graphene on stepped copper substrate, and may have potential applications to control the quality or fine structure of as-grown graphene by controlling the surface topography of copper foil.

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