Contrasting Behavior of Carbon Nucleation in the Initial Stages of Graphene Epitaxial Growth on Stepped Metal Surfaces

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Using first-principles calculations within density functional theory, we study the energetics and kinetics of C nucleation in the early stages of epitaxial graphene growth on three representative stepped metal surfaces: Ir(111), Ru(0001), and Cu(111). We find that on the flat surfaces of Ir(111) and Ru(0001), two C atoms repel each other, while they prefer to form a dimer on Cu(111). Moreover, the step edges on Ir and Ru surfaces cannot serve as effective trapping centers for single C adatoms, but can readily facilitate the formation of C dimers. These contrasting behaviors are attributed to the delicate competition between C-C bonding and C-metal bonding, and a simple generic principle is proposed to predict the nucleation sites of C adatoms on many other metal substrates with the C-metal bond strengths as the minimal inputs.

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Since its first isolation, graphene has attracted rapidly growing research interest because of its various intriguing properties and potential applications in future electronics [1,2]. However, a route towards scalable mass production of quality graphene for industrial use is still lacking. Among many newly developed techniques, epitaxial growth of graphene on metal surfaces offers a promising avenue [3–17]. Large size and good quality graphene samples have been prepared on various metal surfaces [3–9]. The success in transferring the epitaxial graphene grown on Ni and Cu surfaces to insulating substrates makes this method even more attractive [7,9]. Additionally, various aspects about the growth mechanisms of graphene have been revealed in recent studies of representative C-on-metal systems. For example, the growth of graphene on Ir(111) and Ru(0001) substrates is fed by the supersaturated two-dimensional gas of C adatoms, and a multi-C cluster attachment mechanism has been proposed [10–12], with minimal effect of hydrogen [11,13]. On a Cu substrate, graphene is found to grow through a surface adsorption process, while on Ni it occurs through C segregation or precipitation [14].

Despite these preliminary achievements, very little has been revealed about the growth kinetics, especially in the initial nucleation stages of C adatoms. Experimentally it has been found that C nucleation starts from the lower edges of steps on Ir(111) [15] and Ru(0001) [10] surfaces, but it is still unclear why nucleation at the step edges is preferred over terraces. Previous studies of C nucleation on stepped metal surfaces were primarily based on consideration of preferred binding sites of isolated C adatoms (monomers). For example, the observed C nucleation at the step edges on Ni(111) was attributed to the strong binding of C monomers to the lower step edges [18,19]. Determination of nucleation sites is crucial in improving both the quality and quantity of epitaxial graphene. In the growth of graphene on Ru(0001), multiple nucleation on terraces can easily degrade the quality of graphene because defects will form at the interfaces of separately nucleated graphene islands [11]. In graphene growth on Ir(111), the nucleation sites must not be too sparse, because otherwise rotated graphene domains are more likely to grow at the boundaries of the major phase of the islands that are aligned with the substrate [16,17]. Quantity-wise, in order to eventually achieve mass production for industrial applications, it is more desirable for nucleation of graphene islands to take place over the entire substrate rather than only at the edges of preexisting steps. In light of these aspects, a general guiding principle of determining the nucleation sites on different substrates will be highly beneficial.

In this Letter, we present a comparative study of the energetics and kinetics in the initial stages of epitaxial graphene growth on three representative stepped metal surfaces, using first-principles calculations within density functional theory. We find the traditional monomer-based picture of epitaxial growth cannot explain the experimentally observed step edge nucleation of C on Ir(111) and Ru(0001), because the steps on these substrates cannot effectively trap C monomers. Instead, a novel dimer-based picture is proposed, in which the substrate steps can readily facilitate the formation of C dimers at their lower edges. Moreover, the interaction between two adatoms is found to be repulsive on flat Ir(111) and Ru(0001), making ad-dimer formation improbable, whereas it is attractive on flat Cu(111), leading to easy ad-dimer formation. We rationalize these contrasting kinetic behaviors of C adatoms based on the delicate competition between the C-C bonding and C-metal bonding, and generalize this picture to predict the initial growth stages of graphene on different metal substrates.

In our studies, we use the Vienna *ab initio* simulation package (VASP) [20] with projector augmented wave potentials [21] and the generalized gradient approximation (Perdew-Burke-Ernzerhof) [22] for the exchange-correlation functional. All the metal surfaces are modeled by a 6-layer slab, with atoms in the lower 3 layers fixed at their respective bulk positions. We use (322) and (332) surfaces to model the stepped Ir(111) and Cu(111) surfaces, which contain {100} (*A*-type) and {111} (*B*-type) microfacets, respectively. The stepped Ru(0001) surface is modeled by a vicinal surface with its normal along the $\langle 0\bar{1}110\rangle$ direction, which contains alternating *A*- and *B*-type steps. All the terrace widths are ~11–12 Å. The *k*-point mesh used in the calculations is $1 \times 3 \times 1$ for stepped Ru(0001), and $3 \times 3 \times 1$ for all the other cases [23]. We use the climbing image nudged elastic band method [24] to determine the energy barriers of the various kinetic processes.

We first study the adsorption and diffusion of C monomers on flat metal surfaces. We considered the fcc hollow (with an atom directly below in the third layer), hcp hollow (with an atom directly below in the second layer), subsurface octahedral, and subsurface tetrahedral sites for a given system. The most stable adsorption sites and the corresponding binding energies, defined by $\Delta E_{\mathrm{C}} = E_{\mathrm{C/subst}} - E_{\mathrm{C}} - E_{\mathrm{subst}}$, on Ir(111), Ru(0001), and Cu(111) are hcp (−7.44 eV), hcp (−7.66 eV) (in agreement with previous calculations [10,11]), and subsurface octahedral (−5.66 eV), respectively. The stronger binding on the other two substrates and the weaker binding on Cu(111) are consistent with the *d*-band model [25]. On Ir(111) and Ru(0001), the energy in the metastable fcc sites are 0.25 eV and 0.74 eV higher, respectively. On Cu(111), the metastable sites (fcc, hcp, bridge, subsurface tetrahedral) are less stable than the subsurface octahedral sites by ~0.6 eV. The surface diffusion barriers (ε_a) of a C monomer between a stable and the nearest metastable states are 0.75 eV and 0.87 eV on Ir(111), Ru(0001), respectively. On Cu(111), the calculated C monomer diffusion barrier (0.55 eV) is for hopping between octahedral subsurface sites via a tetrahedral subsurface site.

We next investigate the adsorption and diffusion of C monomers at step edges of Ir(111) and Ru(0001). As shown in Fig. 1, the calculated binding energies at step edges are not much larger than those on flat surfaces. The same is true for the kinetic barriers. Considering the high growth temperatures in experiments (~1000 K), we arrive at the conclusion that the substrate steps do not serve as effective traps for C monomers. The absence of large step-crossing barriers and deep wells at step edges, in contrast to the traditional Ehrlich-Schwoebel picture [26–28], is attributed to the difference in passivation of the substrate atoms near step edges by C adatoms [29]. We also note that when compared with the cohesive energy of C atoms in freestanding graphene (−7.94 eV, in agreement with [10,30]) or graphene adsorbed on metal surfaces (slightly higher, [31]), the above energy values for C monomer binding on terraces or around the steps suggest that there is always a strong driving force on the C monomers toward growing into larger graphene sheets if such C islands or adsorbed graphene sheets could first be formed on the surfaces.

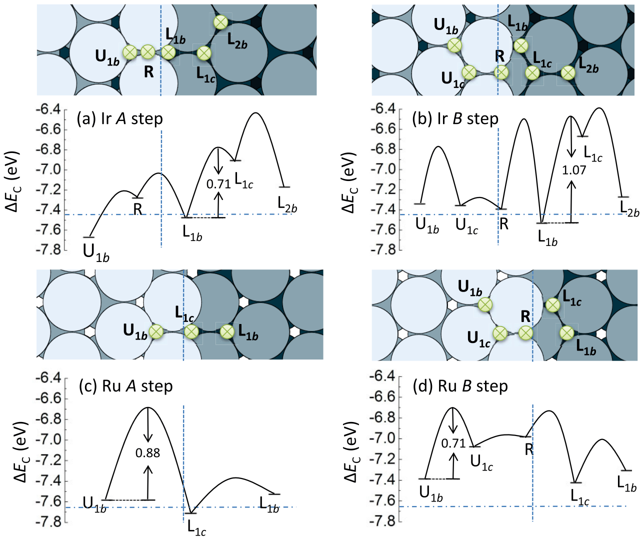

FIG. 1 (color online). Top views of adsorption sites and binding energies of a C adatom around (a) Ir *A* step, (b) Ir *B* step, (c) Ru *A* step, and (d) Ru *B* step. The solid curves represent C diffusion profiles. The vertical dashed line represents the position of the step edge, and the horizontal dash-dotted line indicates the C binding energy on flat surfaces. Definition of labels: U—upper terrace, L—lower terrace, R—ridge site where C only binds to atoms in the ridge of a step edge, *b*—hcp site, *c*—fcc site.

Where should nucleation of C adatoms occur if they are not effectively trapped anywhere on the substrates of Ir and Ru? The above results indicate that knowing the behavior of noninteracting C monomers is insufficient to answer this question. Specifically, since C adatoms are known to form strong covalent bonds with one another when they nucleate to form graphene, it is necessary to take the C-C interaction into account. We therefore next study the formation of C dimers as the first step of nucleation on the metal substrates. Figure 2 shows the trend of binding energies of two C adatoms on the flat metal surfaces, defined by $\Delta E_{2\mathrm{C}} = E_{2\mathrm{C/subst}} - 2E_{\mathrm{C}} - E_{\mathrm{subst}}$, as a function of the separation distance. One can immediately notice that on Ir(111) and Ru(0001) the formation of C dimers is energetically unfavorable, but on Cu(111), dimers are much more stable than separate C adatoms by over 2 eV. Moreover, the energy barrier of forming a dimer for two neighboring C adatoms is only 0.32 eV on Cu(111), which is much smaller than those on Ir(111) (1.37 eV) and Ru(0001) (1.49 eV). These findings suggest that on Ir(111) and Ru(0001), C adatoms are mutually repulsive and cannot form dimers, whereas on Cu(111) they strongly attract each other, leading to the formation of dimers and larger islands.

We next show that, even though on flat Ir and Ru surfaces C dimerization is not preferred, it can be readily

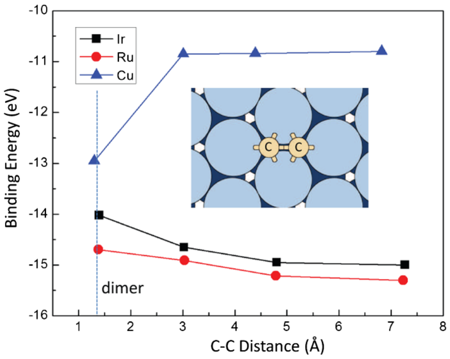

FIG. 2 (color online). Binding energies of two C adatoms on flat metal surfaces as a function of their separation distance. Data points around the vertical dashed line correspond to the formation of C dimers. Inset shows the top view of a C dimer on a close-packed metal surface. Kinetic barriers are not shown.

facilitated by the step edges. In Fig. 3 we plot the binding energies of two C adatoms on stepped metal surfaces with their separation. In all cases, there is a deep potential well upon the formation of a C dimer at lower step edges. This exceptional tendency towards dimerization at substrate step edges is related to the special local bonding geometry of a C dimer at those sites, which is shown in Figs. 3(a) and 3(b). By comparing those with a C dimer on flat surfaces shown in the inset of Fig. 2, one can observe that the C-metal bonds in the latter case are more strongly twisted. Since the covalent bonds are highly directional and it is energetically costly to change the relative bond angles, the relaxation of the covalent bonds by the step geometry leads to the extra stability of the C dimers.

The above results have shown that on Ir(111) and Ru(0001), nucleation of C adatoms first occurs at substrate step edges, in agreement with existing experiments [10,15]; whereas on Cu(111), our results predict that C adatoms should nucleate everywhere on the surface. We note that, once formed on the flat surface of Cu(111), a C dimer can also diffuse relatively freely with an activation barrier of ~0.5 eV [30] to reach a step edge, where it binds more strongly [see Figs. 3(g) and 3(h)]. However, at desirable growth conditions, such C dimers can collect additional C monomers or coalesce to form larger C fragments, and quickly lose their mobility, again leading to fast growth of graphene everywhere on Cu(111).

The contrasting behavior of the interacting C adatoms on flat close-packed Ir(111), Ru(0001), and Cu(111) surfaces can be attributed to the competition between the C-C and C-metal interactions. The C-C bond lengths of C dimers on flat Ir(111), Ru(0001) and Cu(111) surfaces are 1.397 Å, 1.376 Å, and 1.299 Å, respectively, which are very close to the length of a C-C double bond (1.34 Å). A double bond requires two bonding electrons from each C adatom, but one C adatom has only four valence electrons and three nearest metal neighbors on the surface. So intuitively, the formation of a C dimer will weaken the C-metal bonding because of fewer bonding electrons.

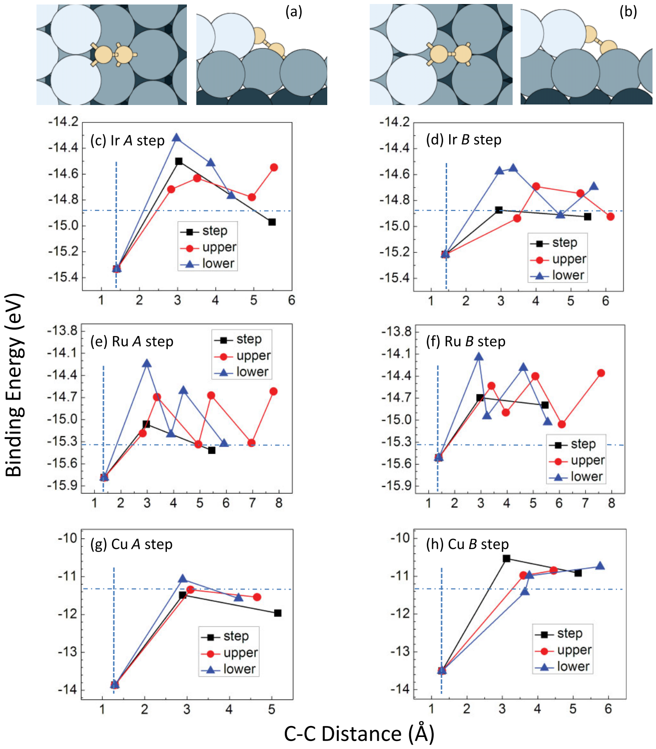

FIG. 3 (color online). (a) and (b) Top and side view of the most stable configuration of a C dimer at the lower edge of a (a) *A* step and (b) *B* step. (c–h) Binding energies of two C adatoms with one C atom fixed at the lower step edge and another placed in stable or metastable sites on upper terraces, on lower terraces, or at the lower step edges, with increasing distances from the first adatom. The horizontal axis is their separation distance. The vertical dashed line in each panel shows where a C dimer is formed, and horizontal dash-dotted line shows the binding energy of two separate C adatoms on flat surfaces.

Therefore, if the C-metal bonds are very strong, which is the case of Ir and Ru, the dimer formation is not energetically favorable. Conversely, in the case of Cu where C-metal bonding is weak, formation of a dimer is preferred for two C adatoms.

Next we show that the above picture is not limited to the three representative cases, but can be generalized into a simple guiding principle. To this end, we compare the binding energies of C monomers and C dimers on the close-packed surfaces of various transition metals, as shown in Fig. 4. It is apparent that the weaker the C-metal interaction is, the more preferred the C dimers are. In all the cases of noble metals, which have closed *d* shells and strong free-electron-like surface states, C dimerization is preferred. The dimer-preferred and dimer-not-preferred systems are essentially separated by the vertical dashed line corresponding to the energy of a C-C double bond (−6.33 eV). The deviation from this trend may be, for example, because of the variation in bonding nature or geometrical effects. Based on the results presented earlier and the prototypical nature of the systems we have studied therein, we can further conclude that for those systems in

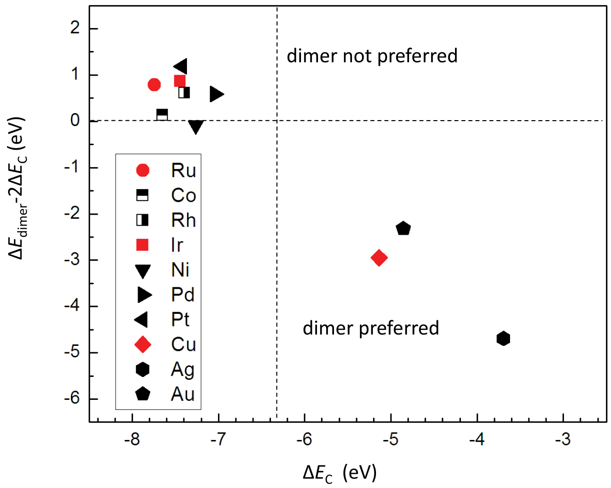

FIG. 4 (color online). Binding energy difference between a C dimer ($\Delta E_{\rm dimer}$) and two C monomers ($2\Delta E_{\rm C}$) with respect to $\Delta E_{\rm C}$ on close-packed transition metal surfaces. The vertical dashed line corresponds to the energy of a C-C double bond (-6.33 eV).

which C dimers are not preferred on terraces, C nucleation should first occur at substrate step edges. Thus, our study makes it possible to predict where the initial nucleation should happen armed solely with the knowledge of the binding energy of C monomers to the metal substrate.

This generic principle can lead to many strong predictions. For example, in the strong C-metal binding regime, a flat substrate with scarce steps may not result in growth of quality graphene because of the simultaneous nucleation at multiple sites on the terraces [10], a somewhat counterintuitive conclusion. In the weak C-metal binding regime, epitaxy on single-crystal flat Cu(111) is more likely to yield graphene with the desired high quality and potential mass production, because C adatoms prefer to nucleate everywhere, and the mismatch of graphene with Cu substrate is very small.

In summary, we have performed a comparative study of the energetics and kinetics of C adatoms on stepped Ir(111), Ru(0001), and Cu(111) surfaces, with intriguing predictions. The present work establishes that one must go beyond the standard monomer-based nucleation and growth picture by explicitly considering where a C-C dimer would prefer to nucleate in uncovering the underlying atomistic mechanisms of the growth of C nanostructures on metal surfaces. The predicted behaviors in the early stages of epitaxial graphene growth are expected to be instrumental in achieving mass production of high quality epitaxial graphene.

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