Formation of Multilayer Cu Islands Embedded beneath the Surface of Graphite: Characterization and Fundamental Insights

Ann Lii-Rosales  
_Iowa State University and Ames Laboratory, ylii@iastate.edu_

Yong Han  
_Iowa State University and Ames Laboratory, y27h@iastate.edu_

James W. Evans  
_Iowa State University and Ames Laboratory, evans@ameslab.gov_

Dapeng Jing  
_Ames Laboratory, djing@iastate.edu_

Yinghui Zhou  
_Ames Laboratory_

See next page for additional authors

Follow this and additional works at: [https://lib.dr.iastate.edu/ameslab_manuscripts](https://lib.dr.iastate.edu/ameslab_manuscripts)

Part of the Chemical Engineering Commons, Materials Science and Engineering Commons, and the Physical Chemistry Commons

Recommended Citation
Lii-Rosales, Ann; Han, Yong; Evans, James W.; Jing, Dapeng; Zhou, Yinghui; Tringides, Michael C.; Kim, Minsung; Wang, Cai-Zhuang; and Thiel, Patricia A., "Formation of Multilayer Cu Islands Embedded beneath the Surface of Graphite: Characterization and Fundamental Insights" (2018). Ames Laboratory Accepted Manuscripts. 125.  
[https://lib.dr.iastate.edu/ameslab_manuscripts/125](https://lib.dr.iastate.edu/ameslab_manuscripts/125)

This Article is brought to you for free and open access by the Ames Laboratory at Iowa State University Digital Repository. It has been accepted for inclusion in Ames Laboratory Accepted Manuscripts by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Formation of Multilayer Cu Islands Embedded beneath the Surface of Graphite: Characterization and Fundamental Insights

Abstract
We present an extensive experimental study of the conditions under which Cu forms encapsulated islands under the top surface layers of graphite, as a result of physical vapor deposition of Cu on argon-ion-bombarded graphite. When the substrate is held at 800 K during deposition, conditions are optimal for formation of encapsulated multilayer Cu islands. Deposition temperatures below 600 K favor adsorbed Cu clusters, while deposition temperatures above 800 K favor a different type of feature that is probably a single-layer intercalated Cu island. The multilayer Cu islands are characterized with respect to size and shape, thickness and continuity of the graphitic overlayer, relationship to graphite steps, and stability in air. The experimental techniques are scanning tunneling microscopy and X-ray photoelectron spectroscopy. We also present an extensive study using density functional theory to compare stabilities of a wide variety of configurations of Cu atoms, Cu clusters, and Cu layers on/under the graphite surface. The only configuration that is significantly more stable under the graphite surface than on top of it, is a single Cu atom. This analysis leads us to conclude that formation of encapsulated Cu islands is kinetically driven, rather than thermodynamically driven.

Keywords
Graphite, copper, intercalation, surface

Disciplines
Chemical Engineering | Materials Science and Engineering | Physical Chemistry

Authors
Ann Lii-Rosales, Yong Han, James W. Evans, Dapeng Jing, Yinghui Zhou, Michael C. Tringides, Minsung Kim, Cai-Zhuang Wang, and Patricia A. Thiel

This article is available at Iowa State University Digital Repository: https://lib.dr.iastate.edu/ameslab_manuscripts/125
Formation of Multilayer Cu Islands Embedded Beneath the Surface of Graphite: Characterization and Fundamental Insights

Ann Lii-Rosales,1,2 Yong Han,1 James W. Evans,1,3,4 Dapeng Jing,1 Yinghui Zhou,1,† Michael C. Tringides,1,3 Minsung Kim,1 Cai-Zhuang Wang,1,3 Patricia A. Thiel1,2,5*

1The Ames Laboratory–USDOE, Ames, Iowa 50011, USA
2Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA
3Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA
4Department of Mathematics, Iowa State University, Ames, Iowa 50011, USA
5Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, USA

Keywords: Graphite, copper, intercalation, surface

Abstract

We present an extensive experimental study of the conditions under which Cu forms encapsulated islands under the top surface layers of graphite, as a result of physical vapor deposition of Cu on argon-ion bombarded graphite. When the substrate is held at 800 K during deposition, conditions are optimal for formation of encapsulated multilayer Cu islands. Deposition temperatures below 600 K favor adsorbed Cu clusters, while deposition temperatures above 800 K favors a different type of feature that is probably a single-layer intercalated Cu island. The multilayer Cu islands are characterized with respect to size and shape, thickness and continuity of the graphitic overlayer, relationship to graphite steps, and stability in air. The experimental techniques are scanning tunneling microscopy and X-ray photoelectron spectroscopy. We also present an extensive study using density functional theory to compare stabilities of a wide variety of configurations of Cu atoms, Cu clusters, and Cu layers on/under the graphite surface. The only configuration that is significantly more stable in the carbon gallery than on the carbon surface, is a single Cu atom. This analysis leads us to conclude that formation of encapsulated Cu islands is kinetically-driven, rather than thermodynamically-driven.

1. Introduction

Intercalation at or near the surface of layered materials is intriguing for several reasons. First, it invokes the possibility of capturing the intercalant in a region sufficiently close to the surface to influence surface properties such as magnetism, transport, friction, and catalysis, while also positioning the intercalant such that it may be protected from oxidation or other environmental damage. Second, the intercalant is likely to be forced into a two-dimensional configuration where surface effects can be maximized (relative to total volume).

* Corresponding author. Email: thiel@ameslab.gov (Patricia A. Thiel)
There have been many recent studies of intercalation between graphene and a non-graphitic support, [1-4] but little attention has been paid to intercalation at the surface of bulk graphite, i.e., between the topmost graphene sheets of many-layer graphene. The alkali metals are a notable exception, where past work has shown that some, but not all, such metals intercalate readily at the surface of graphite.[5, 6] A natural question is whether graphite surface intercalation occurs for other types of metals, and if so, whether it differs from bulk intercalation.

Bulk intercalation is very well-known in graphite, where three families of elemental metals (alkali metals, alkaline earths, and rare earths), as well as many metal complexes, are known to form bulk graphite intercalation compounds (b-GICs).[7] In contrast to the families of metals known to form b-GICs, the elemental transition metals – including Cu – do not form b-GICs, engendering an expectation that surface intercalation should not occur at all. However, behavior for near-surface intercalation can in principle be fundamentally different than for b-GIC’s, as has in fact recently been shown for a few metals including Cu which form near surface multilayer metallic islands.[8] Their intercalation (encapsulation) requires two conditions: Deposition at elevated temperature, and pre-existing defects created by ion bombardment. The latter follows a strategy devised first by Büttner et al. for Cs/graphite.[9] The present paper is a detailed investigation that focuses specifically on the Cu/graphite system, both experimentally and theoretically.

There is great interest in closely-related systems that are of high technological relevance, such as graphene grown on Cu(111) and Cu foil,[1, 10, 11] as well as Cu intercalated between graphene and non-graphitic supports.[12, 13] For instance, Cu is a suitable material for condensation heat transfer (CHT) because of its high thermal conductivity. However, Cu oxidizes when exposed to the atmosphere, resulting in reduced thermal conductivity. The problem can be overcome by coating Cu with monolayer graphene, which is impermeable even to He gas.[14] It has been demonstrated that monolayer graphene not only suppresses Cu oxidation under ambient conditions, it is also wetting-transparent to Cu in the presence of a water droplet.[15] As a result, graphene-coated Cu increases CHT by being oxidation resistant.

The interaction between graphene and Cu is weak, but still strong enough to produce (multiple) moiré patterns on Cu(111). The multiplicity is taken to reflect the weak interaction.[1, 16-18] Besides the weak surface interaction, C has an extremely low solubility in Cu, at only 0.04 atomic% at 1000 °C.[19] There is also no known stable form of solid Cu carbide.[20-22] Such lack of reactivity between Cu and C guarantees a wide temperature range for exploring encapsulation of metallic Cu at the graphite surface.

Elsewhere, we have published a relevant study of Cu deposited on graphite at room temperature.[23] We found that deposition at room temperature resulted in Cu clusters on the terraces that were often unstable during scanning, i.e., easily perturbed and swept away. This is consistent with the weak interaction noted above. Experimental data and theoretical modeling showed that nucleation of Cu islands was dominated by heterogeneous nucleation at defects on graphite terraces. The defects originated from a small fraction of ions (ca. 0.05%) in the otherwise-neutral metal flux, associated with the electron-beam evaporator. We use the same conditions in the present experiments, although here the defects produced by the metal ions are inconsequential in comparison to defects that are produced by argon-ion bombardment of the graphite surface before metal deposition.

This paper is organized as follows. Sec. 2 describes the basic experimental and computational methods. Sec. 3 presents experimental data that focus on the clean graphite surface, the temperature-dependence of Cu growth, the characteristics of encapsulated Cu multilayer
islands, and the stability of these islands upon exposure to atmosphere. Sec. 4 presents theoretical studies which encompass single Cu atoms and small Cu clusters, both adsorbed on top of a graphite surface and intercalated below the graphite surface. They also encompass extended Cu layers. Sec. 5 is a discussion. Some additional details are provided in the SI.

2. Experimental and Computational Methods

_**Experimental methods.**_ Experiments were performed in an Omicron ultrahigh vacuum (UHV) chamber equipped for ion bombardment, physical vapor deposition of metals, STM, and XPS. Samples of highly-oriented pyrolytic graphite, ZYB grade, were cleaved in air, outgassed in UHV at 800 K, ion-bombarded with 3 keV Ar\(^+\) (except when pristine graphite was preserved deliberately), and outgassed again at 900 K, prior to Cu deposition. The Cu flux was on the order of \(10^{14} \text{ nm}^{-2} \text{ s}^{-1}\), and integrated Cu flux was held constant at \(10^2 \text{ nm}^{-2}\) for each deposition. These numbers were based Cu coverage estimated from STM following deposition on the ion-bombarded surface at 800 K, assuming unity adsorption probability. XPS was performed with an Omicron ESCA housed in the same chamber as the STM. Full details about experimental methods are given in the Supporting Information.

_**Computational methods.**_ We performed first-principles density functional theory (DFT) total energy calculations for the Cu-HOPG systems using the plane-wave VASP code.[24-27] The projector-augmented-wave (PAW) method [28, 29] was used for the electron-core interactions, and the optB88-vdW functional [30], was used to approximately account for dispersion interactions. We use the VASP pseudopotentials generated 2013. A variety of benchmark tests were performed for both graphite and Cu, as described in the Supporting Information.

In Sec. 4, we consider two types of Cu+graphite systems. The first involves single atoms or small clusters of Cu. In those calculations, we used a slab consisting of 4 graphene monolayers (GMLs) as the substrate, with fixed bottom layer. There was a 2 nm vacuum thickness along the direction perpendicular to the slab surface, and the lateral size of the supercell was taken to be \(6 \times 6\) in units of the graphite lattice constant, \(a_C\). The \(k\) mesh was \(7 \times 7 \times 1\), and the energy cutoff was 600 eV. The force-convergence criterion was 0.1 eV/nm. The second type of Cu+graphite system involves an extended Cu layer or multilayer. In these calculations, we used a \(1 \times 1\) supercell in units of \(a_C\). This has a Cu-graphite lateral mismatch of \((a_C - a_{Cu}/\sqrt{2})/(a_{Cu}/\sqrt{2})\times100\% \approx -3.9\%\) (a small compressive strain in the Cu film). The thickness of the graphite substrate was taken to be 6 GMLs (with fixed bottom layer). The \(k\) mesh was \(51 \times 51 \times 1\). Vacuum thickness, energy cutoff, and force-convergence criterion were the same as for Cu atoms/clusters.

3. Experimental Results and Discussion


The pristine graphite surface has flat, smooth terraces, as shown in the large-scale STM image in Fig. 1(a). At high magnification, C atoms in the graphite lattice are resolved (Fig. 1(b)). In this image, only half the carbon atoms appear as protrusions. This is a well-known effect due to the existence of two inequivalent subsets of carbon atoms, produced by the A+B-A stacking of carbon sheets.[31-33] The measured lattice spacing is 0.247 ± 0.003 nm (based on a number of
measurements \( x = 20 \), in agreement with the literature value of 0.246 nm.[34] Notably, HOPG is not single-crystal, but rather consists of 1-10 \( \mu m \) grains.[35] Mosaic spread is small along the \( c \)-axis, but large in the (0001) plane.[36] Thus in-plane crystallographic orientations cannot be compared between different STM images.

Defects are generated by subjecting pristine graphite to 3 keV Ar\(^+\) ion bombardment, as shown in Fig. 1(c, c’). The defects appear bright in STM (Fig. 1(d-g)) due to electronic perturbation.[37-42] The features have various shapes and sizes. The height is \( \leq 0.35 \) nm. Single-atom vacancies on graphite are known to produce features with three-fold symmetry in STM, somewhat similar to the image in Fig. 1(e).[9, 39, 43, 44] Other types of features presumably correspond to more complex surface damage, e.g., multiple atom vacancies, interstitial carbon, and/or lattice distortion.[43, 45, 46] Surrounding the defects are regions of HOPG that exhibit a \((\sqrt{3} \times \sqrt{3})R30^\circ\) superlattice, highlighted by the rhombus in Fig. 1(f). This is also well-established as a signature of the electronic perturbation due to damage or adsorption.[37, 41, 47] Based on the images, the number density of sputter-induced defects is \((7.3 \pm 0.4) \times 10^3 \mu m^{-2}\). (Error determination is described in the Supporting Information.)

3.2. Copper Growth at Various \( T_{dep} \).

When Cu is deposited on ion bombarded graphite at \( T_{dep} = 300 \) K and 500 K (Fig. 2(a, b)), the majority of the surface is covered by rough Cu clusters. These tend to be dislodged by the STM tip during scanning, causing streaky images and proving that they represent Cu on top of the graphite surface. We refer to this type of feature as bare Cu clusters.

At \( T_{dep} = 600 \) K, the bare Cu clusters are replaced by smooth stable islands (Fig. 2(c)), ranging from 1.6 nm to 27.6 nm in height. (The range is based on data from 4 different experiments.) The smooth stable islands usually exhibit a faceted, quasi-hexagonal footprint. Detailed views of some of these islands are shown in Fig. 3.

High resolution imaging on top of the faceted islands reveals a structured hexagonal lattice (Fig. 4). The lattice spacing is 0.247 \( \pm 0.003 \) nm (\( x = 30 \)), which matches the spacing measured on the graphite substrate. This value is close to, but significantly different from, the interatomic distance in the (111) plane of bulk Cu, which is 0.256 nm. Therefore, the hexagonal lattice is graphitic. No moiré pattern is observed on top of the islands. The faceted footprints suggest the presence of metallic Cu, and the heights indicate multilayers of Cu. These islands are thus metallic Cu multilayers encapsulated by a graphitic lattice, consistent with their notable stability during imaging. They are termed encapsulated (multilayer) islands.

Smaller, defect-like features co-exist with the encapsulated islands, both on top and beside them (Fig. 3 and 4). Examples are shown at high magnification in Fig. 4(d,e). These features are more defined and rounded than the pre-existing defects in the carbon lattice resulting from ion bombardment (Fig. 1d-g). Their heights are below 1 nm. They are assigned as ion-bombarded defects that are decorated by a few Cu atoms. These features are stable under tunneling conditions, indicating that all of the Cu is in close contact with the graphite defect.

For comparison, Cu deposited on non-ion-bombarded graphite at 600 K is shown in Fig. 2(d). Here the majority of Cu forms small, round clusters that are typically a few nm tall, and are easily dislodged by the tip. There are no encapsulated islands. The existing Cu clusters on terraces are nucleated at defect sites created by Cu ion impact (cf. Sec. 1).[23] The absence of encapsulated
Cu islands shows clearly that Ar ion-bombardment is necessary for their formation. Defects created by Cu ion impact are apparently inadequate.

Having established that 600 K is the onset temperature for Cu to intercalate at the surface of ion-bombarded graphite, we now explore deposition at higher temperatures. Figure 5 shows examples of encapsulated Cu islands formed at \( T_{dep} = 700 \) K and 800 K. As at 600 K, many islands have faceted footprints. The insets in Fig. 5 show atomic resolution of the graphite lattice on top of some Cu islands following growth at 700-800 K, demonstrating that this is a common and robust observation. (In cases where no inset is shown, atomic-scale imaging was simply not attempted.)

For growth in the temperature range 600-800 K, the number density \( (N) \) of bare Cu clusters on top of graphite decreases, relative to the density of encapsulated islands. This is shown by the data in Table 1. Further, the encapsulated islands become somewhat taller and wider with increasing \( T_{dep} \). Temperatures above this range are unfavorable for encapsulated multilayer Cu islands, as discussed below. Hence, under our experimental conditions, 800 K is the optimal growth temperature for producing large encapsulated multilayer islands.

<table>
<thead>
<tr>
<th>( T_{dep} ) (K)</th>
<th>Encapsulated multilayer islands</th>
<th>Bare clusters</th>
<th>Pancakes</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>55 ± 4</td>
<td>14 ± 3</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>31 ± 3</td>
<td>1.0 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>850</td>
<td>1.0 ± 0.4</td>
<td></td>
<td>314 ± 10</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td>318 ± 14</td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td></td>
<td>94 ± 14</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Number densities of encapsulated multilayer Cu islands, bare Cu clusters, and pancakes.

At \( T_{dep} = 850 \) K, the encapsulated islands become much less common, and are replaced by small, diffuse, pancake-like features covered by the graphite lattice (height: 0.25 ± 0.03 nm; width: 12 ± 1 nm; \( x = 1571 \) islands). These are illustrated in Fig. 6(a, c, d, e). Their height suggests that they are a single layer of Cu embedded beneath the graphite surface. Their footprints are round. Encapsulated multilayer islands can also be found occasionally. At 900 K, only pancakes exist, and they have essentially the same dimensions as those grown at 850 K (height: 0.27 ± 0.04 nm; width: 14 ± 2 nm; \( x = 1433 \) islands). Finally, at \( T_{dep} = 1100 \) K, only a few Cu pancakes are observed.

Figure 7 shows a series of XP spectra for \( T_{dep} = 300 \) K to 900 K. The binding energy of the Cu \( 2p_{3/2} \) peak is constant at 932.74 ± 0.05 eV, consistent with metallic Cu.[48] The full-width at half-maximum, 1.82 ± 0.01 eV, also shows no significant variation in this sequence. Hence, these quantities are not sensitive to the changes in Cu structure that occur in this temperature range, though evidence of different Cu states might be achievable with higher energy resolution.

In summary, a progression of Cu morphologies is observed when Cu is deposited on the ion-bombarded graphite surface. At \( T_{dep} = 300 \) K to 500 K, there are bare Cu clusters on top of the surface. Starting at 600 K, large encapsulated islands appear, and by 800 K these have almost completely replaced the bare clusters. Starting at 850 K, pancakes appear, and by 900 K pancakes have completely replaced the encapsulated multilayer islands. At \( T_{dep} = 1100 \) K, the density of pancakes is much lower. Cu also decorates the ion-bombardment-induced defects, giving rise to small features that are similar to, but distinguishable from, bare defects.
3.3. Further Characterization of Encapsulated Multilayer Cu Islands.

**Shapes and sizes.** Profiles in Fig. 3 and Fig. 5 indicate that two shapes are possible for the encapsulated multilayer islands, one with flat tops and one with round tops. At $T_{\text{dep}} = 600$ K to 800 K, there are roughly equal numbers of each. The round islands tend to be taller than the flat islands. This is illustrated by Fig. 8, which is a histogram of flat and round islands, sorted by height, in a single experiment. We hypothesize that round tops signal poorer atomic order in the Cu islands, at least at the top, or a higher step density.

Atomic resolution of the overlying carbon lattice is obtained much more easily on flat-top islands than on round-top islands. An explanation may be that the flat type provides an ordered platform of Cu that supports the carbon lattice. In contrast, the round type is atomically disordered or has a high step density, which makes the graphitic overlayer difficult to image. This interpretation is supported by a report of C$_{60}$ intercalated between graphene and Cu(100), where atomic resolution of graphene is obtained for crystalline (well-ordered) C$_{60}$, but not for amorphous (disordered) C$_{60}$.[49]

Observations of flat vs. round-top multilayer islands suggest the possibility of discontinuous transitions between distinct equilibrium shapes for varying control parameters (island size, etc.) This would be somewhat analogous to behavior for strained semiconductor quantum dots.[50]

Dimensions of flat-top encapsulated islands formed at 800 K are plotted in Fig. 9. The diameter of the flat top ($d$), scales poorly with island height ($h$), while the width of the sloping side ($a$), scales closely with $h$. These dimensions are defined in the inset to Fig. 9(a). The ranges of values (all in units of nm) are $34 < d < 607$, $1.5 < h < 43$, and $3.9 < a < 165$. The average aspect ratio ($d/h$) is $17 \pm 9$, and the average slope of the side ($h/a$) is $0.24 \pm 0.03$ ($x = 55$ islands for both values). Many of the islands are sufficiently large to be imaged with other techniques. For instance, scanning electron microscopy (SEM) images are shown in the SI.

**Continuity of the graphitic overlayer.** A large multilayer island (36 nm tall), formed by deposition at 800 K, is shown in Fig. 10(a,a'). Remarkably, a high magnification image on the sloping island side (indicated by a white square in the derivative image) also reveals a perfect graphitic lattice (Fig. 10(c)), indicating that the carbon sheet extends continuously from the substrate to the top of the island, even with such a massive island.

**Role of steps.** It is not unusual to find islands where a graphite step cuts across the top. Figure 11 shows examples at high magnification; others can be seen in Fig. 5 and Fig. 12. To all appearances, the step has no relationship to the island’s shape or position, suggesting that the step played no role in the island’s formation. For instance, the island does not emanate from the step in the up-going direction, which would have indicated that the step served as an entry portal.

**Thickness of the graphitic overlayer.** Islands crossed by steps can provide information about the thickness of the graphitic overlayer. To this end, closer examination of the steps is warranted to ascertain that they are truly graphite steps (rather than Cu steps), especially on the island tops. Figure 11(b,d,f) shows profiles of steps atop 3 islands, and also in adjacent regions with no island. In each case, the height of the step on the island-free region is the same as its height on the island top. Furthermore, the height of the step in Fig. 11(a) is 0.341 nm, which corresponds to a graphene monolayer (GML). (Other step heights are close to integral multiples of this number.) For comparison, the spacing between [111]-type planes in Cu is 0.208 nm, so a Cu-Cu step can be ruled out. Finally, the graphite lattice can be imaged on both sides of the step on top of the island (as in Fig. 5(b), for example), hence proving that Cu is covered by graphitic layers on both sides.
Combined, these observations show unambiguously that the steps crossing islands are continuous graphite steps.

If the height of a graphite step, in units of GMLs, is \( g \), then the number of GMLs atop the Cu island on the thicker (upper) side of the step is at least \( g + 1 \), because the height on the thinner (lower) side is at least 1. Figure 11(e) shows an island for which \( g = 3 \) (the largest value observed), indicating that the upper part of this Cu island is covered by 4 or more GMLs. The full range of observations is \( 1 \leq g \leq 3 \) (\( x = 10 \) islands). We conclude that Cu islands can be covered, partially or entirely, by multiple GMLs.

It is conceivable that multilayer Cu islands intersected by steps would be different than islands on terraces, in terms of the thickness of the graphitic overlayer. To test this possibility, we examine the large island in Fig. 10(a), which is not crossed by a step. On top of this island, we obtain atomic-scale resolution (in the area outlined by a white rectangle) of the carbon lattice as shown in Fig. 10(h). Two noteworthy pieces of information emerge from these images.

First, there is a boundary (dashed line in Fig. 10(h)) that separates two different regions. The boundary does not propagate parallel to the horizontal scan direction, so we can rule out the possibility that it is due to tip effects. To the left of the boundary (enlarged in Fig. 10(d)), the carbon lattice appears as triangular arrays of bright spots. As noted in Sec. 3.1, this is a common phenomenon where only 3 out of 6 carbon atoms are imaged as bright spots in STM.[32, 33] In contrast, to the right of the boundary (enlarged in Fig. 10(f)), the 6 carbon atoms are more equally imaged as bright spots, resulting in bright hexagonal honeycombs. The difference in these two regions is further shown in corresponding line profiles just below Fig. 10(d,f). In these profiles, equal intensities of adjacent bumps indicate that all 6 carbon atoms are imaged equivalently, producing a honeycomb. This condition is nearly met in the profile on the right. We have evidence that these two types of regions are also present on the sloping side of the island.

Second, the boundary separating the two regions is not a step. According to a study of epitaxial graphene on Cu(111),[17] monolayer graphene is imaged as honeycombs in STM. If the honeycomb region atop the large Cu island is monolayer graphene, and the other is multilayer graphene, there should be an apparent step that separates the two regions. Instead, we observe a buckling similar to that reported in the transition area between AC/AB stacking of bilayer graphene.[51, 52] Buckling (or rippling) in bilayer graphene is a means of accommodating and releasing strain energy in the presence of dislocations.[51, 52] In our case, it is reasonable to interpret the two different regions of carbon lattice as AB stacking (left region in Fig. 10(d)), producing 2 sets of inequivalent carbon atoms, and AA stacking (right region in Fig. 10(f)), where all carbon atoms are aligned to reveal hollow honeycombs. Thus there must be at least 2 GMLs on top of this island.

The buckling in Fig. 10 has a maximum amplitude of 0.086 nm, about 10 times lower than the value reported in Ref. [51, 52]. This discrepancy may be due to different types of shifting (e.g., AB/AC, AB/AA) and/or different graphene-substrate interactions in the two studies.

In summary, two types of experimental data lead to the conclusion that multilayer Cu islands can be covered by multiple GMLs: (1) the continuous graphite steps that cross some islands; and (2) evidence of a carbon stacking fault on top of an island with no crossing step.
3.4. Air Exposure.

In order to determine if graphite encapsulation protects multilayer Cu islands from oxidation or contamination under ambient conditions, a sample was prepared by Cu deposition at 800 K. STM and XPS were performed prior to exposure. The sample was then transferred from the UHV chamber, into atmosphere, at room temperature for ~30 minutes. After air exposure, the sample was transferred back into the UHV chamber for further characterization. First, XP spectra of the sample were taken. Second, the sample was outgassed at 800 K for 20 minutes (identical to the routine outgassing parameters described in Section 2). More XP spectra were taken after outgassing, followed by STM imaging.

Figure 12 shows images of encapsulated Cu islands before (a, b) and after (c, d) air exposure. As evident from the images, the morphology of islands (both flat and round top) persists after air exposure and outgassing. The islands are not affected by the ambient conditions nor outgassing at 800 K – one would not be able to differentiate STM images of the islands before and after air exposure. Island heights after air exposure fall in the range of heights before exposure, suggesting that no significant coarsening occurred due to outgassing. The islands are very stable during imaging, and imaging was not rendered more difficult due to these treatments. The atomically-resolved C lattice is also observed atop islands, identical to the as-deposited Cu islands.

XPS provides additional insight into the changes in chemical composition due to air exposure. As seen in Fig. 12(e, f), XPS shows metallic Cu on the as-deposited sample with the Cu 2p$_{3/2}$ peak at 932.8 eV. After air exposure (but before outgassing) the spectrum exhibits a mixture of metallic and oxidized Cu signal with a narrow Cu 2p$_{3/2}$ peak at 932.8 eV (43\% of the total peak area), a broad peak at 934.3 eV (57\% of the total peak area) and a more pronounced shake-up satellite. The oxidized Cu signal disappears due to desorption upon annealing. The position of the broad Cu 2p$_{3/2}$ peak, and the shape of the shake-up satellite, are most consistent with Cu(OH)$_2$.[53] The O 1s region from the air-exposed sample can be deconvoluted into two components. One, with a peak at 531.0 eV, is also consistent with Cu(OH)$_2$.[54] The second, at 532.3 eV, is attributed to adsorbed water molecules. Furthermore, the assignment of Cu(OH)$_2$ is also supported by the standard heats of formation. At -449.8 kJ/mol, Cu(OH)$_2$(cr) is more than two times lower, and thus more favored to form, than CuO$_{(cr)}$ at -157.3 kJ/mol or Cu$_2$O$_{(cr)}$ at -168.6 kJ/mol.[55]

The oxidized Cu component makes a large contribution to the total Cu 2p$_{3/2}$ signal immediately after air exposure, which we attribute mainly to water adsorption and dissociation at the Cu atoms present on top of the surface, pinned at defect sites (Fig. 4(d,e)). These co-exist with the large Cu islands and, because their emitted photoelectrons suffer little or no attenuation, they can constitute a large fraction of total Cu signal.

In summary, the encapsulated multilayer islands survive air exposure very well. This is in agreement with previous reports of oxidation resistance of Cu-rich substrates, which include Cu foil and Cu/Ni alloys, as a result of growing a graphene overlayer via chemical vapor deposition.[15, 56]
4. Computational Results and Discussion

4.1. DFT calculations for Cu atoms and clusters adsorbed on, or intercalated in, graphite.

To determine whether it is more favorable for Cu atoms to be adsorbed on top of a graphite surface or intercalated beneath the top GML(s), we analyze systems with \( n \) Cu atoms adsorbed on or intercalated in a graphite slab. We define the chemical potential of a Cu atom in a cluster interacting with graphite as

\[
\mu_{\text{Cu}} = \frac{E_{\text{tot}} - E_{\text{graphite}}}{n} - E_{\text{Cu}}
\]

where \( E_{\text{tot}} \) is the total energy of the Cu cluster plus graphite, \( E_{\text{graphite}} \) is the energy of relaxed graphite substrate, \( n \) is the total number of Cu atoms in the Cu cluster, and \( E_{\text{Cu}} \) is the energy of one Cu atom in gas phase. This chemical potential accounts for both interaction between Cu atoms, and for Cu-C interaction. Lower chemical potential corresponds to a more stable configuration.

For one adatom (\( n = 1 \)) adsorbed on the substrate, \( \mu_{\text{Cu}} \) reduces to the conventional adsorption energy \( E_{\text{ads}} = E_{\text{tot}} - E_{\text{graphite}} - E_{\text{Cu}} \).

Let us first consider the adsorption energies of a single Cu adatom on top of graphite after relaxation from the seven initial positions TH, TT, HT, BM, MB, MM, and CC, defined in Fig. 13. The most favorable adsorption site is TH with \( E_{\text{ads}} = -0.500 \) eV, in agreement with an earlier determination of the most-favored site.[23] The adsorption energies at other sites, TT, BM, and HT, are -0.495, -0.494, and -0.337 eV, respectively. Adsorption of the Cu atom at MB, CC, and MM sites is unstable, and the adatom moves to a local minimum close to the initial site after full relaxation. Thus, the minimum energy path for diffusion of the adatom will be from TH to BM to TT, then to another TH site via BM. The lower limit of the diffusion barrier (\( E_{\text{diff}} \)) is about 0.005 eV. These values of \( E_{\text{ads}} \), and the minimum value of \( E_{\text{diff}} \), differ from values reported previously (0.589 eV and 0.020 eV, respectively[23]) where a different functional (optPBE) was used for the exchange and correlation energy.

Now we assess the energies of one Cu atom placed beneath the top GML. We find that the intercalated Cu atom for any of seven initial sites in Fig. 13 has no significant lateral movement after full relaxation, and the energies are very close to each other, from the lowest, -1.000 eV at CC, to the highest, -0.936 eV at HT. Therefore, for a single Cu atom, intercalation is 0.5 eV more favorable than adsorption on top of the graphite surface.

More detailed DFT results for single Cu atoms, both adsorbed and intercalated, are given in Table S1 of the Supporting Information.

The geometries of small Cu clusters (\( n = 2 \) to 5), both adsorbed and intercalated, are shown in Fig. 14. The initial configurations are described in the Supporting Information. Some trends are noteworthy. First, three of the adsorbed clusters (\( n = 2, 3, 4 \)) rearrange upon relaxation so that only one of the Cu atoms is in contact with the graphite surface, at a BM site. The other cluster (\( n = 5 \)) maintains three Cu atoms in contact with graphite, arranged in a triangle at adjacent TH sites. In the \( n = 5 \) cluster, one of the atoms also moves up out of contact with the graphite. Thus, there is a strong tendency to reduce or minimize contact between the Cu cluster and the graphite surface.

In contrast, the intercalated clusters always maintain Cu-Cu bonds parallel to the surface, though the position and bond length can change relative to the initial geometry. The intercalated
clusters cause small bumps in the top GML. For instance, \( h \) (as defined in Fig. 9) is 0.039 nm for \( n = 2 \), 0.086 nm for \( n = 3 \), and 0.083 nm for \( n = 4 \).

Figure 15 provides a plot of \( \mu_{\text{Cu}} \) vs. \( n \) for adsorption and intercalation of the above Cu clusters with \( n = 1 \) to 5. Values are given in Table S2 of the Supporting Information. Surprisingly, while intercalation is strongly preferred for a single atom, intercalation is less favorable than adsorption for \( n = 2 \), 3, 4, and 5 by a wide margin—the energy differences exceed 0.5 eV. The small intercalated clusters exhibit weak intra-cluster binding since their chemical potential is comparable to that for atoms, and in fact the intercalated dimer is unstable against dissociation. In contrast, the adsorbed dimer is far more stable than the adsorbed Cu atom. This reflects formation of a strong Cu-Cu bond of strength 2.65 eV which even exceeds that calculated for a gas-phase Cu dimer, 2.29 eV.

In summary, these DFT calculations show that a single Cu atom adsorbs weakly on top of graphite, but is much more stable when intercalated beneath the surface. The potential energy surface for the intercalated configuration is extremely smooth, and the diffusion barrier is probably very small. When placed on top of the carbon surface, small clusters of Cu atoms tend to adopt 3D configurations that minimize contact with the graphite surface. When placed beneath the top carbon layer, clusters adopt flat configurations but are much less stable than adsorbed counterparts. Hence, intercalation is only thermodynamically favorable for the single Cu atom.

4.2. DFT calculations for complete Cu layers adsorbed on, or intercalated in, graphite.

We also consider systems with a complete Cu layer (i.e., slab or film) supported on and intercalated in graphite. We still use Eq. (1) to calculate \( \mu_{\text{Cu}} \), where the Cu cluster should be understood as a Cu film. The thickness of the Cu film is denoted \( L \) in units of Cu(111) atomic monolayers. Figure 16 and Table 2 give \( \mu_{\text{Cu}} \) as a function of \( L \) for Cu films adsorbed on and intercalated in graphite, as well as two freestanding Cu slabs.

Figure 16 shows that all values of \( \mu_{\text{Cu}} \) approach (the negative of) the bulk cohesive energy with increasing \( L \), as they must, since interfaces exert less influence on the total energy of the Cu film as \( L \) increases. The energies of the freestanding Cu slabs are always higher than the others, showing that a Cu film is stabilized by adsorption or intercalation relative to a freestanding Cu slab. However, values of \( \mu_{\text{Cu}} \) vs. \( L \) are very close, when comparing adsorbed and intercalated Cu films (G0-tTH vs. G1-tTH). The difference is 18 meV or less, i.e., there is little or no significant driving force for intercalation of an extended Cu layer. Further, having one GML vs. two GMLs on top of the Cu film makes no significant difference in the energetics (compare G1-iCC vs. G2-iCC), nor does a shift of bottommost Cu atoms from TH sites to CC sites (G1-tTH vs. G1-tCC). The latter result is unsurprising in light of the very flat potential energy surface for intercalated Cu atoms presented in Sec. 4.1.

Heights (\( h \)) of the intercalated films, relative to the height of the clean graphite slab before intercalation, are shown in Table S3. For \( L = 1 \), the height of the most stable configuration is 0.297 nm. This compares favorably with the measured height of the pancakes (Sec. 3.1), 0.25-0.27 nm, supporting the assignment of pancakes as intercalated single layer of Cu.
Table 2. DFT data for $\mu_{\text{Cu}}$ (in units of eV) vs. Cu film thickness $L$ (in units of GML) for adsorption and intercalation of Cu films, corresponding to Fig. 16.

<table>
<thead>
<tr>
<th>$L$</th>
<th>G0-tTH</th>
<th>G1-tTH</th>
<th>G1-iCC</th>
<th>G2-iCC</th>
<th>Unstrained Cu film</th>
<th>Strained Cu film</th>
</tr>
</thead>
</table>

5. DISCUSSION

Many interesting issues arise from this work. One is the fact that (at least some of) the multilayer Cu islands are covered by multiple graphene sheets. The reason for this is not clear. However, it may account for the fact that moiré patterns are not observed atop encapsulated Cu, even though moirés are observed for encapsulated islands of other metals, notably Dy and Ru.[8] Also, as stated in Sec. 1, multiple moiré patterns have been reported for systems with a single GML on bulk Cu(111). [1, 16-18] The absence of moirés in the present work may be due to the fact that multiple GMLs cover the encapsulated Cu islands (cf. Sec. 3.2), reducing the undulations of the graphitic overlayer.

Another interesting issue is the relationship between the defects, the multilayer islands, and the single-layer islands. The density of multilayer islands is roughly 0.5% that of the defects, while the density of single-layer islands is roughly 4%. Originally, Büttner et al.[9] suggested that such defects act as entry portals, with only a few being large enough to allow passage of a metal atom with reasonably low barrier. They based this interpretation on DFT calculations of Cs atoms passing through clean graphite defects. We postulate that the situation is more complex, in the sense that defects may well be decorated with strongly-bound Cu atoms, which could prevent other Cu atoms from being trapped at the defect, hence decreasing the barrier for Cu atom passage. Essentially, in this picture, passage of a Cu atom from the surface into the graphite galleries (or vice-versa) requires a large defect passivated by Cu atoms around the edge. Passage through the pore requires breaking Cu-Cu bonds, but this can be easier than breaking the strong C-Cu bond of the metal atoms directly on the pore’s edge. Strong Cu atom bonding at clean graphite defects is very plausible, given the abundant evidence for strong, preferential transition metal bonding at graphene vacancies[57, 58] and graphite steps.[23]

A related point is the nature of the activated processes which underlie the temperature dependence of multilayer island growth (favored at 600-800 K) and single-layer island growth (favored at 850-900 K). The onset temperatures for these two processes, 600 K and 850 K, correlate approximately with the onset of two processes involving Cu islands adsorbed on top of a pristine graphite surface: coarsening (500 K), and desorption (900 K).[59, 60] We speculate that below 600 K on the ion-bombarded surface, Cu atoms are caught at defects and block them. This leads to 3-dimensional surface growth, as observed in experiment. Above 600 K, Cu-Cu bonds
can be broken at large defects, which effectively allows some Cu atoms to pass through, even while Cu atoms around the rim remain trapped at low-coordinated carbon sites.

The DFT results for complete layers show no significant thermodynamic preference for intercalation versus adsorption. Thus, occurrence of the former must be interpreted as a kinetic phenomenon. Of key significance is the substantially lower $\mu_{\text{Cu}}$ for an isolated intercalated atom relative to an isolated adatom on the top surface. If we assume that transport of such isolated Cu atoms between the gallery and the top surface is reasonably facile, then there is some degree of equilibration between the densities of these two species (both of which are supersaturated due to deposition). A traditional nucleation theory for critical size $i$ would assign the nucleation rate as $K_{\text{nuc}} \sim h N_i N_i^*$. Here $N_i \sim \exp(E_i/(k_B T)) (N_i)^i$ is the density of critical clusters of $i$ atoms (which is regarded as being in quasi-equilibrium with the adatom density according to this Walton relation), and $E_i > 0$ is the binding energy of such clusters. $N_i$ is significantly enhanced in the gallery versus on the surface, which naturally enhances the chance of nucleation. Despite this feature, the weak binding of small clusters in the gallery relative to the surface (as demonstrated in Fig. 15) would counter this effect for small critical sizes (i.e., $E_i$ would be far smaller for intercalated than for surface islands). However, the results of Fig. 16 indicate that if one extrapolates the results of Fig. 15 to much larger cluster sizes, the curves for adsorption and intercalation must merge. Thus, for larger critical sizes, $E_i$ would be comparable for intercalated and surface islands, and the enhanced $N_i$ in the gallery would lead to a dominance of nucleation of intercalated versus surface islands. Developing a quantitative model based upon these ideas, and consistent with the experimental data, is the subject of ongoing work. This model would also assess locations for nucleated islands relative to defects.[61]

This scenario is fundamentally different than that for Dy intercalation, where we have previously shown (via DFT) that intercalated layers are significantly more stable than adsorbed layers. Hence, it appears that different energetic scenarios may apply to different metals but give rise to similar intercalation phenomena.

5. Conclusions

In summary, a progression of Cu morphologies is observed when Cu is deposited on the ion-bombarded graphite surface. At $T_{\text{dep}} = 300$ K to 500 K, bare Cu clusters exist on top of the surface. Starting at 600 K, large encapsulated multilayer islands appear, and by 800 K these have almost completely replaced the bare clusters. Starting at 850 K, single-layer Cu pancakes appear, and by 900 K pancakes have completely replaced the encapsulated multilayer islands. At $T_{\text{dep}} = 1100$ K, the density of pancakes is much lower. Cu also decorates the ion-bombardment-induced defects, giving rise to small features that are similar to, but distinguishable from, bare defects. In XPS there is a single Cu $2p_{3/2}$ peak consistent with metallic Cu, i.e., different chemical states of Cu are not resolved in these experiments.

Careful examination of the encapsulated multilayer Cu islands shows that some have flat tops, while others have round tops, with the latter presumably signaling atomic disorder or a high step density. For both types, diameter exceeds height, the average aspect ratio being $17 \pm 9$ for flat-top islands. The graphitic lattice can be resolved on the sloping sides of the multilayer islands as well as on the tops, showing that graphene layers drape continuously over the island. Graphitic steps sometimes cut continuously from the graphite substrate across tops of islands, with no evidence that the step played a role in island formation. From the heights of these steps, we infer that some or all of the Cu islands are covered by multiple graphite layers. The presence of an apparent stacking fault in the graphitic overlayer on top of an island supports this conclusion.
STM and XPS show that the encapsulated multilayer islands survive air exposure very well. There is evidence of some Cu(OH)$_2$ after air exposure, but the oxidized Cu signal in XPS disappears when the air-exposed sample is heated to 800 K in UHV.

DFT calculations show that a single Cu atom adsorbs weakly on top of graphite, but is much more stable when intercalated beneath the surface. The potential energy surface for the intercalated configuration is extremely smooth, and the diffusion barrier is probably very small. When placed on top of the carbon surface, small clusters of Cu atoms tend to adopt 3D configurations that minimize contact with the graphite surface. When placed beneath the top carbon layer, Cu clusters adopt flat configurations but are much less stable than adsorbed counterparts. Hence, intercalation is only favorable for the single Cu atom. Calculations for extended Cu layers show that there is no strong driving force for intercalation of this configuration either. We conclude that Cu atoms penetrate, then become trapped by nucleation within the galleries. In other words, Cu encapsulation appears to be a kinetic effect rather than a thermodynamic one.

Acknowledgments

This work was supported mainly by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. Research was performed at the Ames Laboratory, which is operated by Iowa State University under contract # DE-AC02-07CH11358. DFT was performed, in part, with a grant of computer time at the National Energy Research Scientific Computing Centre (NERSC). NERSC is a DOE Office of Science User Facility supported by the Office of Science of the U.S. DOE under Contract No. DE-AC02-05CH11231. The experimental work was performed or supervised by ALR, DJ, YZ, MCT, and PAT. Theoretical work was performed or supervised by YH, JWE, CZW, and MK. YZ’s participation in the experimental effort was supported by the China Scholarship Council. JWE’s participation in the theoretical work was supported by the DOE, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.

Present Addresses

† Collaborative Innovation Center for Optoelectronic Semiconductors and Efficient Devices, Department of Physics, Xiamen University, Xiamen 361005, China.

REFERENCES


Figure 1. STM images of pristine and ion-bombarded graphite, at low and high magnification. The low-magnification images are shown in both topographic and derivative forms. Derivative images allow defects to be seen more clearly at low magnification. (a) Topographic and (a’) derivative images of pristine graphite at low magnification. (b) Topographic image of graphite at high magnification. A (1×1) unit cell is marked by a rhombus. (c) Topographic and (c’) derivative images of a graphite surface treated with 3 keV Ar⁺ ion bombardment, then annealed at 900 K for 2 hours to remove embedded Ar gas. (d-g) Topographic images of defects due to ion bombardment. The (√3×√3)R30° superstructure is marked by a rhombus in (f). Tunneling conditions are: (a) +1.1 V, 0.23 nA; (b) +70 mV, 0.25 nA; (c) +1.1 V, 0.23 nA; (d) +20 mV, 0.45 nA; (e) +40 mV, 0.45 nA; (f) +70 mV, 0.25 nA and (g) +15 mV, 0.45 nA.
Figure 2. STM images of Cu deposited on (a) ion bombarded graphite at 300 K, (b) ion bombarded graphite at 500 K; (c) ion bombarded graphite at 600 K, and (d) pristine graphite at 600 K. Tunneling conditions are: (a) +4.8 V, 0.23 nA; (b) +4.7 V, 0.22 nA; (c) +4.6 V, 0.25 nA; (d) +4.3 V, 0.30 nA.
Figure 3. (a-d) Topographical STM images of intercalated Cu islands in the graphite surface at 600 K. (a’-d’) Corresponding 3-dimensional images. (e-h) Line profiles of the islands measured from topographical images. Tunneling conditions are: (a) +4.6 V, 0.27 nA; (b) +4.7 V, 0.27 nA; (c) +4.7 V, 0.27 nA; (d) +4.4 V, 0.27 nA.
Figure 4. (a) STM image of Cu islands formed at 600 K with its derivative image shown in (a’). High-resolution images of carbon lattice obtained directly on top of the island on the upper left (island height is 1.80 nm) is shown in (b), and carbon lattice atop the island on the lower right (island height is 1.77 nm) is shown in (c). (d) Defect-like features with resolved carbon lattice on top of an intercalated Cu island from a different experiment than (a). (e) A defect-like feature on graphite substrate around an intercalated Cu island from the same experiment as (d). Tunneling conditions are: (a) +4.3 V, 0.26 nA; (b) +0.13 V, 0.49 nA; (c) +0.13 V, 0.49 nA; (d) +0.9 V, 0.46 nA; (e) +3.8 V, 0.24 nA.
Figure 5. STM images of intercalated Cu islands at (a-c) 700 K and (d-i) 800 K. Insets to (a, b, d, e, and h) are high-resolution images that show the carbon lattice on top of islands. All insets are 5 nm × 5 nm, except for the one in (b), which is 7 nm × 7 nm. Line profiles of islands, shown at right, are designated with image labels. Profile (i) is drawn in red to match the scale of red y-axis on the right. Tunneling conditions are: (a) +3.8 V, 0.24 nA; (b) +3.8 V, 0.24 nA; (c) +4.7 V, 0.24 nA; (d) +4.5 V, 0.27 nA; (e) +4.3 V, 0.27 nA; (f) +5.0 V, 0.26 nA; (g) +4.3 V, 0.27 nA; (h) +4.3 V, 0.26 nA; (i) +4.2 V, 0.24 nA.
Figure 6. STM images of intercalated Cu at (a-b) 850 K and (c-e) 900 K. (a, b) show small Cu pancakes. (a’, b’) are derivative images. At this low magnification (500 nm × 500 nm), all dot-like features – which are especially visible in the derivatized images – are small pancakes. (b) shows a large round multilayer island in the presence of small Cu pancakes that are more visible in the derivative image in (b’). (c, c’) shows small Cu pancakes only. (d, d’) A close-up image of the small pancakes, and (e, e’) shows a pancake, from (d) indicated by a white box, that is atomically resolved, including defects on top of the pancake and also on the graphite substrate. (e”) is a 3D image and (f) is an associated line profile for (e). Tunneling conditions are: (a) +4.6 V, 0.22 nA; (b) +4.6 V, 0.22 nA; (c) +4.7 V, 0.23 nA; (d) +3.9 V, 0.29 nA; (e) +0.44 V, 0.39 nA.
Figure 7. XPS data following deposition of Cu on ion-bombarded graphite. $T_{dep}$ is indicated. The vertical line shows the average binding energy of the Cu $2p_{3/2}$ peak, 932.74 ± 0.05 eV. Take-off angle is 0° with respect to the surface normal. Intensities are normalized to the Cu $2p_{3/2}$ peak.

Figure 8. Height histograms of flat (blue; 5.68 ± 2.73 nm) and round (orange; 9.17 ± 2.76 nm) Cu islands from a single experiment at 800 K. Flat islands are shorter than round ones in general, with some overlap in the distributions (orange bars are made slightly transparent to show overlapped blue ones). Percentages of flat and round islands are about 53% ($x = 66$ islands) and 47% ($x = 58$ islands), respectively. Bin size is 1.5 nm for both histograms.
Figure 9. Plots of (a) island top width vs. island height and (b) rim width vs. island height for flat top islands ($x = 55$ islands) at 800 K. Inset to (a) is a schematic of an encapsulated island with dimensions labeled (see text). Inset to (b) shows an enlarged region indicated by the red box, up to island height of 10 nm and rim width of 50 nm. Note the high $R^2$ value (0.983) that reflects the close relationship between rim width and island height. Lines in both plots are forced to go through the origin.
Figure 10. STM images of (a) of an encapsulated multilayer Cu island produced at 800 K, (a’) its derivative image, and (b) associated line profile. (c) shows the carbon lattice on the slope of the island, as indicated by a square in (a’). (h) is a topographical image of the carbon lattice directly on top of the island, in the area marked by a rectangle. The slight buckling of the surface is shown in the line profile in (i). (h’) is a Fourier-transformed image of (h). The dashed line in (h’) separates two regions of carbon lattice, which are zoomed in to show the (d) triangular arrays and (f) honeycombs, with distinctly different line profiles in (e) and (g). Tunneling conditions are: (a) +4.8 V, 0.21 nA; (c) +0.08 V, 0.40 nA; (d, f, h) +0.04 V, 0.39 nA.
Figure 11. STM images of intercalated Cu islands that are cut by a step on the graphite substrate. Black and green arrows denote line profiles for the step on island and on graphite substrate, respectively. The graphite step heights, in units of GMLs, are: (a, b) $g = 1$, island height is 1.88 nm; (c, d) $g = 2$, island height is 4.37 nm; and (e, f) $g = 3$, island height is 5.16 nm. Three-dimensional view in (a’, c’, e’) also shows the step running over islands. Tunneling conditions are: (a) +0.17 V, 0.46 nA; (c) +4.3 V, 0.24 nA; (e) +4.1 V, 0.27 nA.
Figure 12. (a, b) STM images of intercalated Cu islands as deposited at 800 K. (c, d) STM images of intercalated Cu islands after ~30 minutes air exposure and outgassing at 800 K for 20 minutes. (a’, b’, c’, d’) Corresponding derivative images. (e) Intensity normalized Cu 2p XP spectra of (black) as deposited, (blue) air exposed and (red) vacuum outgassed after air exposure of Cu deposition on sputtered HOPG. Peak fitting shows (dotted) metallic Cu and (dashed) Cu(OH)_2 components. (f) O 1s XP spectrum of air exposed Cu deposition on sputtered HOPG. Peak fitting shows O signal from Cu(OH)_2 at 531.0 eV and adsorbed H_2O at 532.3 eV. Take-off angle is 45° with respect to the surface normal. Range of island heights in (a) is 3.21 – 8.37 nm, (b) in 3.67 – 15.25 nm, (c) is 3.36 – 9.25 nm, and (d) is 3.37 – 9.92 nm. Tunneling conditions are: (a) +4.7 V, 0.30 nA; (b) +4.7 V, 0.30 nA; (c) +4.7 V, 0.22 nA; (d) +4.2 V, 0.23 nA.
**Figure 13.** Top view of seven initial positions (TH, TT, HT, BM, MB, MM, and CC) of a Cu atom with the graphite substrate for DFT calculations. The letters T, H, B, M, and C stand for top, hollow, bridge, midpoint, and center, respectively. The first letter denotes the location with respect to the first (top) GML, and the second letter denotes location with respect to the second (lower) GML. TH, BM, TT, and HT are denoted elsewhere as $T_\alpha$, B, $T_\beta$, and H, respectively. [57]

**Figure 14.** (a)-(g) Top and side views of geometries for the systems of Cu clusters ($n = 2$ to 5) plus a graphite substrate after full relaxation from our DFT calculations. Gray balls represent C atoms, and red balls represent Cu atoms.
Figure 15. $\mu_{\text{Cu}}$ vs. $L$ for $n = 1$ to 5. Values are given in Table S1.

Figure 16. $\mu_{\text{Cu}}$ vs. Cu film or slab thickness $L$, for adsorbed and intercalated Cu films. Values are given in Table 2. Freestanding Cu slabs are represented by curves labeled “unstrained Cu slab” and “strained Cu slab.” The latter configuration has a strain of -3.9% to match $a_C$. The other four configurations are adsorbed Cu films. G0-tTH means that there is no GML on top of the adsorbed Cu film, and the bottom-most Cu atoms are at TH sites on top of the graphite surface. G1-iTH means that a Cu film is intercalated beneath one GML and the bottommost Cu atoms of the Cu film are at TH sites at the graphite interface. Other films are named analogously. Four curves overlap almost completely: G0-tTH, G1-iTH, G1-iCC, and G2-iCC. Values are given in Table 2. The horizontal red dashed line denotes $-E_{\text{coh}}$ for bulk fcc Cu.