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From carbon atom to graphene on Cu(111): an ab-initio study

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Abstract. Graphene growth by chemical vapor deposition on copper is one of the most popular method to obtain large scale sample. If the commensurability of graphene with Cu(111) plays a determinant role, the most stable geometries for the 2D crystal do not correspond to the most stable adsorption sites of individual carbon atoms on the same surface. In this paper, we analyzed this contradiction based on density functional theory calculations. From the three stable sites for isolated carbon atoms on Cu(111), only two of them are involved when small clusters of carbon are adsorbed. However, because of the shift from strong C-Cu interaction for isolated (or unsaturated C atoms) to weak van der Waals C-Cu bonding, other stable geometries are found for adsorbed infinite graphene. We propose here two new stable graphene adsorption geometries and we present a detailed analysis of the various adsorption geometries.

1 Introduction

Since its discovery [1], graphene has developed a wide interest among scientific community due to its unique electrical, mechanical and thermal properties [2,3]. Graphene can be obtained by mechanical exfoliation, graphitisation of the substrate or chemical vapor deposition (CVD) technique. CVD of hydrocarbon on transition or noble metal [4–11] has proven to be the most powerful technique to grow graphene over large areas, opening the field to potential applications in nanoelectronics [12,13].

The interaction of perfect graphene with metallic substrate can be divided into two classes: strong bonds for Co, Ni and Pd and weak bonds for Ag, Au, Cu, Pt or Al [14]. For what concerned graphene/Cu system, there is only a 4% mismatch between the honeycomb lattice of graphene (lattice constant of 2.46 Å) and the Cu(111) surface nearest-neighbor distance of 2.55 Å [15] which makes the Cu(111) surface a good candidate for the CVD production of graphene. It has therefore been widely used [9–11], as well as other surface orientations [16,17].

The electrical, mechanical and thermal properties of graphene depend also significantly on the orientation and density of the grain boundaries [18–20], providing a way to engineer polycrystalline layers for different applications. A rough model is the following: during growth, the graphene forms islands of different orientations and morphologies that merge together involving the formation of grain boundaries. A microscopic modeling of this phenomenon is however still missing. In particular, the existence of several stable interface geometries could play a key role in the grain boundaries formation. The role of

hydrogen in the CVD growth of graphene has been emphasized and it has been shown that hydrogenation of graphene cluster edges helps for the diffusion of carbon atoms under the top layer [21]. We do not consider hydrogen in the present work since only the initial growth stage is investigated.

Several ab initio calculations have already been performed to determine metal/graphene interface [14,22], in particular for the Ni(111) [23,24] and Cu(111) interface geometry [24–27]. For Ni/graphene interface, the growth of graphene occurs after diffusion of carbon atoms from Ni bulk to the Ni surface and six (meta)stable configurations were found [23,24] based on local density approximation (LDA) and van der Waals (vdW)-corrected functional. For Cu/graphene interface, no carbides are formed and only surface processes are involved. For the latter system, Xu and Buehler [25] calculated within the LDA three different stable geometries, namely *fcc-hcp*, *top-fcc* and *top-hcp*, with one of them (*fcc-hcp*) clearly less stable (adsorption site and interface geometries are described in Figs. 1 and 3). Adamska et al. [24] predict that *bridge* (or *b*) structures may also play a role.

For single carbon atom on Cu(111) surface, three adsorption sites were found with similar energies (*hcp*, *fcc* and *b_{top}*) [26,27] and diffusion barriers between these positions were evaluated to 0.1 eV. The *top* site was found considerably less stable (by 1.5 eV) for individual atoms on Cu(111) in apparent contradiction with the findings that the most favorable Cu/graphene interface geometry involves *top* carbon positions. These results can be partly reconciled thanks to the LDA calculations of Mi et al. [26] that predict that the binding energy per atom of carbon clusters on Cu decreases with the number of atoms

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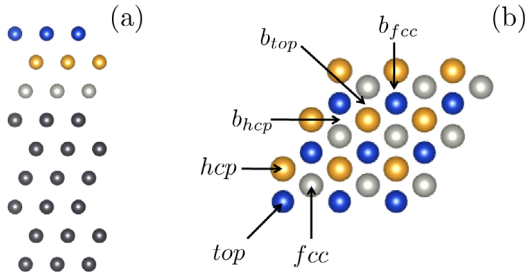


Fig. 1. Supercell used to model the Cu(111) surface. (a) Side view of the supercell. The atoms of the first three Cu layers are displayed with blue, grey and yellow colors (b) top view of the supercell. The *top*, *hcp* and *fcc* adsorption positions correspond to carbon atoms on the top of the first, second and third Cu layer, respectively. Other positions (b_{top} , b_{hcp} and b_{fcc}) correspond to the mid-point between the first *top*, *hcp* and *fcc* sites.

and that, at the same time, the carbon-metal distance increases.

In light of this review of the literature and because of the difficulty to compare results obtained with different levels of approximations, a systematic study of the binding or adsorption energies of carbon on Cu is necessary. We present here density functional theory calculations of graphene growth on Cu(111) within the generalized gradient approximation and the local density approximation. We consider the adsorption of single carbon atom, small clusters of carbon and perfect graphene sheets on Cu(111). We confirm that the more stable graphene adsorption geometries on Cu(111) are not directly related to the most stable adsorption sites of individual carbon atoms and we propose new alternative geometries. This apparent contradiction is related to the increase of the van der Waals character of the carbon-surface bonding as the size of the graphene cluster increases.

2 Method

Plane wave supercell calculations were carried out to model perfect graphene sheets on Cu(111) substrate by using the VASP5.3 code [28,29] with the projector augmented wave method [30] (PAW). We applied the standard C and Cu PAW-potentials [30] from the VASP5.2 database. Cu 3*d* electrons were treated as valence electrons. The valence wave functions were expanded by plane waves, where the corresponding kinetic energy cut-off $E_{cut} = 420$ eV was applied to converge the total energy within a 1 meV precision. We used the generalized gradient approximation (GGA) in the parameterization of Perdew-Burke-Ernzerhof [31] (PBE) and the LDA approximation [32] without spin polarization if not otherwise stated. The smearing scheme in the electronic relaxation was the first order Methfessel-Paxton method [33]. The geometry was optimized with the conjugate-gradient algorithm until the forces were less than 0.02 eV/Å. We used a $5 \times 5 \times 1$ Monkhorst-Pack grid [34] to sample the Brillouin zone.

In previous studies on Cu/C systems LDA [24–26], PBE [27] and van der Waals corrected GGA functional [24] have been used. It is known that PBE underestimates van der Waals binding energies for carbon systems while LDA gives a better estimation. For example, a debonding of graphene on Ni was found with PBE [23]. Also, vdW corrected GGA functional gives bonding energy of graphene on Cu lower than the thermal energy at ambient temperature [24]. For the sake of comparison with the literature, we performed both PBE and LDA calculations. LDA energies are compatible with the observed stability of graphene on Cu at ambient temperature. We have also tested vdW-corrected GGA functional using the optB86b-vdW functional [35] with the same conclusions as for LDA-based calculations (see below), as confirmed by the results of reference [22].

For single carbon and small cluster calculations, we used 82-atom and 89-atom supercells corresponding respectively to 1 and 8 C atoms on top of a 9 monolayer thick Cu(111) surface. For perfect graphene sheet, we used a 99-atom supercell corresponding to a perfect graphene sheet of 18 C atoms on top of a 9 monolayer thick Cu(111) surface.

The perfect Cu(111) surface is given in Figure 1. We used a vacuum layer of 20 Å in the direction normal to the slab to represent isolated slab-boundary condition. We obtain a PBE equilibrium bulk copper lattice constant of 3.63 Å and a LDA equilibrium bulk copper lattice constant of 3.55 Å which agrees well with the experimental lattice constant $a_0 = 3.61$ Å [15]. The GGA calculations were done using the PBE lattice constant whereas the LDA calculations were done using the LDA lattice constant. For C atoms on Cu(111) surface, we have considered different adsorption sites: *top* (on top of the first Cu layer), *fcc* (on top of the third Cu layer), *hcp* (on top of the second Cu layer) and b_{top} (between two *top* sites), b_{hcp} (between two *hcp* sites) and b_{fcc} (between two *fcc* sites) as described in Figure 1.

For infinite graphene on Cu(111), we have found six stable geometries: the usual structures *fcc-hcp*, *top-fcc*, *top-hcp* and the bridge structures, first proposed for Ni(111) surface [23]: *bridge-fcc*, *bridge-hcp* and *bridge-top*. These structures correspond to b_{top} - b_{hcp} , b_{top} - b_{fcc} and b_{hcp} - b_{fcc} , respectively (Fig. 1). For these structures, we set the initial graphene sheet height at 3 Å. The atomic positions of the first bottom Cu layer were fixed and the other atomic positions were fully relaxed.

The binding energy per carbon atom of a C_n cluster on Cu(111) is obtained with:

$$E_b = 1/n \left(E_{C_n/Cu(111)}^T - E_{Cu(111)}^T - E_{C_n}^T \right) \quad (1)$$

where $E_{Cu(111)}^T$ is the total energy of the relaxed Cu(111) substrate, $E_{C_n/Cu(111)}^T$ is the total energy of the C_n cluster on the Cu(111) substrate, $E_{C_n}^T$ is the total energy of the isolated C_n cluster. This definition is the equivalent to the usual adsorption energy for C atom on Cu(111) if $E_{C_1}^T$ is replaced by μ_C , the chemical potential of an

Table 1. Adsorption energy E_b and height h of a C atom on Cu(111) as calculated within PBE and LDA. The values are compared with the PBE adsorption energy E_b of reference [27].

Site	E_b [eV]	h [Å]	E_b [eV]			h [Å]		
			PBE	LDA	Ref. [27]	PBE	LDA	Ref. [27]
<i>top</i>	-0.64	1.52	-	-3.77	-	1.54	-	
<i>b_{top}</i>	-4.87	0.86	-4.94	-5.99	-	0.85	-	
<i>fcc</i>	-4.93	1.05	-4.99	-6.04	-	1.02	-	
<i>hcp</i>	-4.88	1.04	-4.94	-5.98	-	1.00	-	

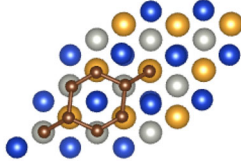


Fig. 2. Top view of the 8-carbon atom cluster supercell after relaxation. Large balls correspond to Cu atoms (see Fig. 1 for detailed description) and small brown balls correspond to C atoms with C-C bonds represented by sticks.

isolated spin polarized C atom. $E_b < 0$ then means that the configuration is stable.

3 Results and discussion

The binding energies E_b for single C atom adsorption are given in Table 1. Only four stable sites have been found in good agreement with the existing values in the literature for PBE functional [27]. Our E_b is between 0.5 eV and 1 eV lower than the data reported in reference [26]. This difference can be attributed to the use of different thickness of Cu slab. As reported by others [26,27], the *fcc* site is the most stable but *hcp* and *b_{top}* sites have very similar adsorption energies where the one of the *top* position is more than 2 eV above but still stable. The b_{hcp} (b_{fcc}) position converge to *fcc* (*hcp*) site, respectively.

Secondly, we have investigated the stability of 8-atom graphene islands on top on Cu(111) surface with different starting structures, including *fcc-hcp*, *top-fcc*, *top-hcp* and *bridge* cases. The small 8-atom cluster is made of a complete 6 carbon atoms ring (Fig. 2). All the initial geometries relax to the same *fcc-hcp* (with the *top* position at the center of the hexagon) geometry. This is coherent with stable *fcc* and *hcp* sites for individual atoms compare to the *top* position and with the hexagonal symmetry requirement for the carbon ring. The binding energy per carbon (E_b) atom is -0.96 eV (average height $h = 1.53$ Å) within PBE and -1.71 eV ($h = 1.49$ Å) within LDA. E_b is then much lower than the adsorption energy found for a single C atom where the distance from Cu substrate is much larger. This finding is similar to the one of reference [26] for a chain of carbon and is related to the switch from covalent C-Cu bonds for single C to a partially van der Waals character of the C-Cu interaction for small C cluster.

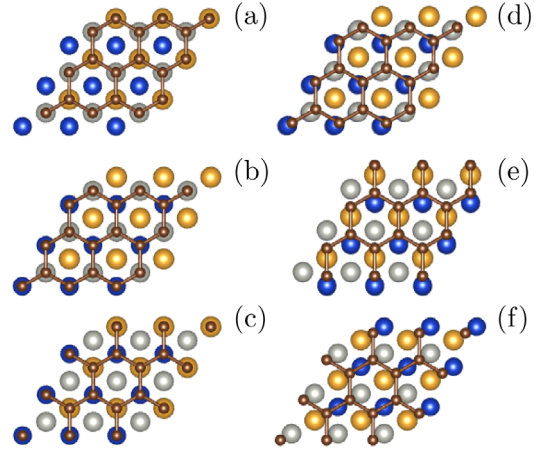


Fig. 3. Top view of graphene sheets on Cu(111) after relaxation. Supercells (a) to (f) correspond to *fcc-hcp*, *top-fcc*, *top-hcp*, *bridge-fcc*, *bridge-hcp* and *bridge-top*, respectively.

We now turn to perfect graphene sheets on Cu(111). The relaxed supercells within LDA are given in Figure 3. Besides the most studied *fcc-hcp*, *top-fcc* and *top-hcp* structures (Figs. 3a–3c), three other interface geometries present local minima: *bridge-fcc*, *bridge-hcp* and *bridge-top*. For the first three, no noteworthy in-plane relaxation from the initial positions have been found. For the initial positions involving *bridge* structures, a relaxation parallel to the surface occurs and the final positions are given in Figures 3d–3f. Similar interface geometries were named *almost-top-almost-fcc* for *bridge-fcc*, *almost-fcc-almost-hcp* for *bridge-hcp* for Ni/graphene system [23]. We will keep the name associated with the initial positions for simplicity. We already note that the *bridge-fcc* and *bridge-hcp* positions are proposed for the first time as stable interface configuration for Cu/graphene systems.

For all graphene sheets considered, we obtain an average C-C nearest-neighbor distance $d = 1.45$ Å close to a perfect isolated graphene sheet. The structural parameters are given in Table 2. Compared to the perfect Cu(111) substrate, the Cu substrate coordinates are barely affected by the graphene sheet. For PBE, the total energies of the systems are nearly degenerated and the minimum of E_b is found for the *top-fcc* geometry. However, all the systems present a positive binding energy and are then unstable. Within PBE, it is therefore thermodynamically more favorable to form a free-standing graphene sheet far from the Cu(111) in contradiction with experiment. This is a well-known artifact of the PBE [22]. Within LDA, as expected, negative binding energies are obtained for all the considered geometries and it is energetically favorable to form a graphene sheet on copper in agreement with experiment. We have also tested vdW-corrected GGA functional [35]. For perfect graphene sheets on Cu(111), binding energies of the order of -70 meV and a ground state geometry *top-fcc* were found but with very similar energy difference between metastable configurations which do not modify the present conclusions. In the following, we discuss LDA results.

Table 2. Comparison between PBE and LDA results for a perfect graphene sheet on Cu(111). Binding energy E_b per carbon atom, average height h between the graphene sheet and the first Cu layer and d_i the average distance between layers i and $i + 1$ counting from the top Cu layer. The structural parameters of the perfect relaxed Cu(111) substrate are given for comparison.

Supercell	E_b [meV]	h [Å]	d_1 [Å]	d_2 [Å]	d_3 [Å]
PBE					
<i>fcc-hcp</i>	578	3.81	2.08	2.10	2.10
<i>top-fcc</i>	576	3.63	2.08	2.10	2.11
<i>top-hcp</i>	577	3.71	2.07	2.10	2.10
<i>bridge-fcc</i>	579	4.05	2.08	2.10	2.11
<i>bridge-hcp</i>	578	3.71	2.07	2.09	2.10
<i>bridge-top</i>	576	4.07	2.07	2.09	2.10
Cu(111)	–	–	2.08	2.09	2.10
LDA					
<i>fcc-hcp</i>	–28	3.33	2.00	2.02	2.03
<i>top-fcc</i>	–39	3.06	2.00	2.02	2.03
<i>top-hcp</i>	–38	3.12	2.00	2.02	2.03
<i>bridge-fcc</i>	–38	3.04	2.00	2.02	2.03
<i>bridge-hcp</i>	–35	3.14	2.00	2.02	2.02
<i>bridge-top</i>	–37	3.12	2.00	2.03	2.03
Cu(111)	–	–	2.00	2.02	2.02

The ground state is found for the *top-fcc* geometry whereas *fcc-hcp* is the less stable by 11 meV/C atom. This relative stability is in agreement with other studies, as well as the small E_b difference with *bridge-top* geometry [24,25]. The –39 meV/C atom for *top-fcc* geometry can be converted to $E_b = -14.40$ meV/Å^{–2} (height $h = 3.06$ Å) which compares well with the LDA values (–13.19 meV/Å^{–2} and 3.26 Å) of Xu and Buehler [25]. Two new adsorption geometries (*bridge-fcc* and *bridge-hcp*) are here predicted with very similar energy than the stable geometries reported earlier [24,25]. *bridge-fcc* is even the second more stable geometry with only 1 meV/atom difference with *top-fcc*, which is well below the uncertainties of the DFT calculations.

The low E_b and large C-Cu distance for graphene is related to the switch from Cu-C covalent interaction to van der Waals interaction, since the C atoms are now sp_2 hybridized and no valence electrons are then available to form a chemical bonding with the Cu d -electrons. This finding has been already evidenced in reference [26] for carbon linear chain to explain the efficiency of graphene growth on polycrystalline Cu. It also rationalizes the finding that the *fcc-hcp* geometry is not the only stable configuration and that local minima are found for 5 other lateral positions.

4 Conclusion

We have performed density functional theory calculations of graphene on Cu(111). We propose two new stable geometries, involving the *bridge* structures, for the graphene

on Cu(111) with binding energies only a few meV per carbon atom less stable than the ground state *top-fcc*. Calculations on single carbon atoms and small clusters show that the *top* site is unfavorable and that *fcc-hcp* sites are preferred. Those results can be reconciled if, during the initial steps of graphene growth, the C atoms are trapped by the *fcc* and *hcp* sites to form *fcc-hcp* islands. When the islands reach sufficient sizes, the Cu - graphene interaction weakened [26] and the graphene can shift to other configurations, e.g. *top-fcc*, with small energy differences. The evaluation of the critical size at which a change of adsorption configuration can be thermally activated is beyond the scope of the study because of the required computational means.

In conclusion, the three stable adsorption sites of single C atom (*hcp*, *fcc*, *b_{top}*) lead to only one stable geometry for small C cluster (*hcp-fcc*). On the other hand, when graphene is formed, several metastable geometries are found and can be thermally activated. Both steps (formation of cluster from individual adsorbed C atoms and diffusion of large graphene cluster) can imply the formation of grain boundaries during growth process.

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