



# Ab initio simulation of diamond epitaxial growth on copper

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## Abstract

Density functional theory calculations show that epitaxial diamond films can be grown on copper substrates due to small mismatches in the copper and diamond lattice parameters and to the absence of their chemical affinity. The mean cohesive energy for (100) films is larger than that for (111) films. However, the (111) films are more stable than the (100) ones in respect to separation from the copper substrate.

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## 1. Introduction

Copper seems to be a promising candidate as a substrate material for epitaxial growth of diamond films. First, its lattice parameter (3.608 Å) is similar to that of diamond (3.567 Å). Second, it has no carbon affinity. Therefore, there is a set of experimental works on this subject [1–9]. The main result of these studies is that diamond crystallites grown on polycrystalline copper can mount up to the 20 μm thickness with the preferable orientation of (111). However, as far as it is known, there is no theoretical support for such experimental studies. The present work is devoted to the ab initio study of geometry and energy peculiarities of diamond epitaxy on copper.

## 2. Method and details of calculations

The calculations were performed using the FHI96md simulation code [10] based on the density functional

theory, pseudopotential method, and the plane wave basis set. The generalized gradient approximation (GGA) in the Perdew and Wang form (PW91) [11] for the exchange and correlation functional and fully separable Troullier–Martins pseudopotentials [12] were employed. The pseudopotentials were constructed using the FHI98pp code [13]. They were verified to avoid ghost states and to describe the basic experimental characteristics of the bulk materials. The *d* component of the pseudopotential for carbon and the *s* component for copper were adopted as local ones. I used the (0.25, 0.25, 0.00) point for the *k* space integrations for slabs, whereas the gamma point was applied for bulk calculations; the energy cut-off of 40 Ry was used in all calculations.

The equilibrium lattice constant  $a_0$  and bulk modulus  $B_0$  calculated for diamond, using Murnaghan equation of state [13], are equal to 3.57 Å and 450 GPa, respectively. They agree well with the experimental values of 3.567 Å and 442 GPa [14].

The (111) and (100) surfaces of Cu were represented by five-layers slabs with the 2 × 2 surface unit cell separated by 20 Å thick vacuum space, and only the first

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surface layer atoms of Cu were relaxed. To avoid the artificial electrostatic dipole field, which arises from the asymmetry of the slab, I used a dipole correction [15].

In order to compare the energetic preferences of different carbon phases and carbon–copper systems I calculated the mean cohesive energy per carbon atom,  $E_{\text{coh}}(\text{mean})$ :

$$E_{\text{coh}}(\text{mean}) = E(C_a) - \frac{E(\text{Cu} - \text{C}) - E(\text{slab})}{N_C}, \quad (1)$$

where  $E(\text{Cu} - \text{C})$  is the energy of the Cu–C system consisted of the Cu-slab and  $N_C$  atoms of carbon;  $E(\text{slab})$  is the energy of the Cu-slab,  $E(C_a)$  is the energy of an isolated C atom. For comparison I have calculated cohesive energies for bulk graphite and diamond: they are 8.74 eV and 8.55 eV, respectively. These values overestimate experimental data (7.37 eV for graphite and 7.35 eV for diamond [16]). This is a usual overestimation of the DFT local density approximation (LDA) and GGA calculations for carbon materials [17–20]. The calculated C–C bond distances are 1.43 Å for graphite and 1.55 Å for diamond compared with the experimental values of 1.42 Å and 1.53 Å, respectively. The equilibrium graphite inter-planar distance has been found to be 8.65 Å. This value is much larger than the experimental one (6.708 Å). However, it is a typical GGA overestimation: see for instance Ref. [21]) where the value of 8.946 Å has been reported.

The mean cohesive energy  $E_{\text{coh}}(\text{mean})$  includes deposits from internal, surface and interface carbon atoms. Obviously, the internal bonds must be more similar to the bulk bonds than others. In order to compare the C–C bonding in the internal atomic layers of the epitaxial films with that of bulk diamond, I have calculated the internal cohesive energy  $E_{\text{coh}}(\text{int})$  using the following expression:

$$E_{\text{coh}}(\text{int}) = \frac{E(\text{Cu} - \text{C})_L - E(\text{Cu} - \text{C})_{L+2} + 2 \times N_C(\text{layer}) \times E_C}{2 \times N_C(\text{layer})}, \quad (2)$$

where  $N_C(\text{layer})$  is the number of carbon atoms in a monoatomic layer.

### 3. Results and discussion

To study the geometry and energetic features of the diamond epitaxial growth on copper surfaces I constructed  $L$ -monolayers diamond films ( $L$  was varied from 2 to 13) in contact with the Cu(100) and Cu(111) surfaces, respectively (see Figs. 1 and 2). In the (111) case the atoms of the bottom C layer were placed in threefold sites (above the centers of Cu triangles), whereas in the (100) case they were positioned in the bridge sites (above pairs of Cu atoms).

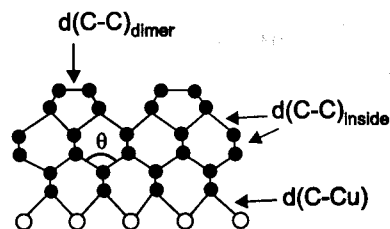


Fig. 1. An atomic scheme of the epitaxial diamond film on the Cu(100) surface.

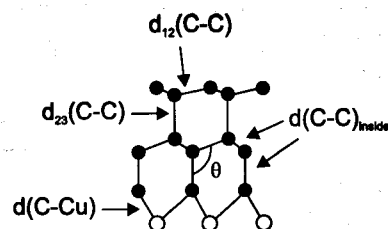


Fig. 2. An atomic scheme of the epitaxial diamond film on the Cu(111) surface.

It has been found that in both the cases the epitaxial films kept their diamond-like atomic geometry with the tetrahedral bonding. Their surface reconstructions and relaxations are similar to those of free diamond surfaces. Namely, the surface of the (100) film is dimerized. The dimer length is 1.38–1.41 Å, similar to 1.37 Å obtained for the bulk diamond (100)- $2 \times 1$  surface by the LDA [22] and quasi-particle [23] calculations. For the (111) relaxed surface I have obtained the surface C–C distance  $d(\text{C} - \text{C})_{12}$  of 1.50–1.51 Å and the undersurface C–C distance  $d(\text{C} - \text{C})_{12}$  of 1.50–1.51 Å, close to the values of 1.46 Å and 1.68 Å, reported by Kern et al. [22] for the bulk diamond (111) surface. Details of data on the calculated interatomic distances and tetragonal angles  $\theta$  are collected in Tables 1 and 2.

As it follows from Tables 1 and 2, the geometry parameters for epitaxial diamond films are in satisfactory accordance with those for bulk diamond (especially for the (111) case).

Calculated values of the cohesive energy,  $E_{\text{coh}}(\text{mean})$  and  $E_{\text{coh}}(\text{int})$  for C(100) and C(111) epitaxial films formed on the Cu(100) and Cu(111) surfaces are plotted in Fig. 3. One can see that  $E_{\text{coh}}(\text{internal})$  approaches

Table 1  
Geometry parameters for the C(100)/Cu(100) epitaxial system

The number of carbon atomic layers ( $L$ )	2	4	6	8	10	12
$d(\text{C} - \text{Cu})$ , Å	1.90	1.95	1.95	1.94	1.94	1.94
$d(\text{C} - \text{C})_{\text{inside}}$ , Å	–	1.56	1.58	1.57	1.56	1.56
$d(\text{C} - \text{C})_{\text{dimer}}$ , Å	1.41	1.40	1.39	1.38	1.38	1.38
$\theta$ , degree	–	122.0	112.3	110.1	109.8	109.7

Table 2  
Geometry parameters for the C(111)/Cu(111) epitaxial system

The number of carbon atomic layers ( <i>L</i> )	3	5	7	9	11	13
$d(\text{C}-\text{Cu}), \text{\AA}$	1.94	1.97	1.95	1.94	1.94	1.94
$d(\text{C}-\text{C})_{\text{inside}}, \text{\AA}$	–	1.57	1.56	1.56	1.55	1.55
$d(\text{C}-\text{C})_{12}, \text{\AA}$	1.50	1.50	1.50	1.51	1.51	1.50
$d(\text{C}-\text{C})_{23}, \text{\AA}$	1.55	1.72	1.71	1.70	1.70	1.70
$\theta$ , degree	104.2	109.6	109.4	110.2	109.9	109.6

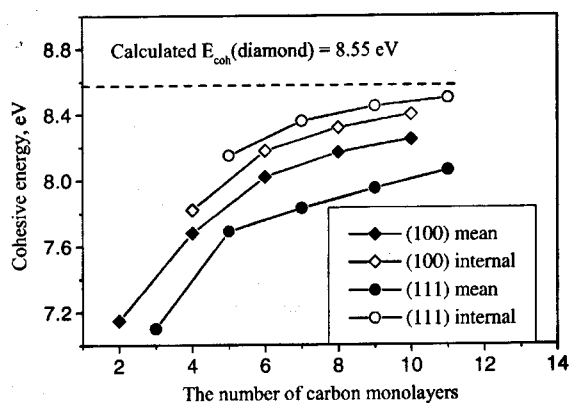


Fig. 3. The cohesive energy (mean and internal) for C(100) and C(111) epitaxial films as a function of the number of carbon monolayers.

the calculated cohesive energy for diamond (8.55 eV) rather better than  $E_{\text{coh}}(\text{mean})$ .

To study the stability of the film-substrate bonding I have calculated the film-substrate adhesion energy  $E_{\text{adh}}$ :

$$E_{\text{adh}} = \frac{E(\text{Cu} - \text{C}) - [E(\text{slab})_{\text{frozen}} + E(\text{film})_{\text{frozen}}]}{N_{\text{C}}(\text{interface})}, \quad (3)$$

where  $N_{\text{C}}(\text{interface})$  is the number of the interface carbon atoms. Energies of the separated Cu-slab,  $(E(\text{slab})_{\text{frozen}})$ , and C-film  $(E(\text{film})_{\text{frozen}})$ , have been calculated for the same atomic geometries as they were found for the corresponding carbon/copper systems.

The  $E_{\text{adh}}$  values characterize the bonding between the carbon film and the copper substrate when they are contacted. However, if we want to study the energetics of the film-substrate separation we need to take into account the relaxation of the carbon film and the copper slab after their separation. The energy difference (per interface atom) between the epitaxial carbon-copper system and the relaxed separated carbon film and the relaxed copper slab can be named the separation energy  $E_{\text{sep}}$ :

$$E_{\text{sep}} = \frac{E(\text{Cu} - \text{C}) - [E(\text{slab})_{\text{relaxed}} + E(\text{film})_{\text{relaxed}}]}{N_{\text{C}}(\text{interface})}. \quad (4)$$

It should be noted that positive values of  $E_{\text{sep}}$  correspond to the energetic advantage for the separation of the epitaxial diamond film from the copper substrate.

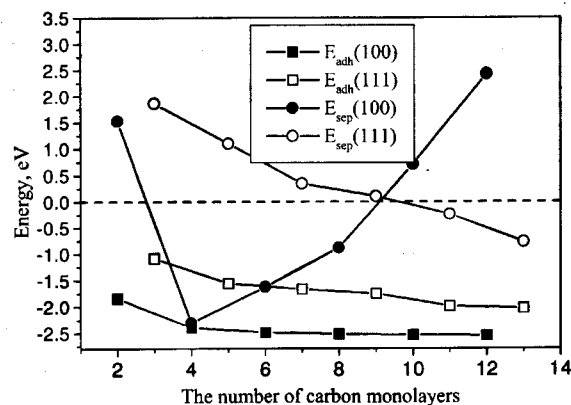


Fig. 4. Adhesion and separation energies for epitaxial diamond films formed on Cu(100) and Cu(111) substrates.

Dependencies of  $E_{\text{adh}}$  and  $E_{\text{sep}}$  on the number of carbon monolayers are plotted in Fig. 4 for both the C(100)/Cu(100) and C(111)/Cu(111) systems. One can see that the energy of the bonding of the diamond epitaxial film with the copper substrate ( $E_{\text{adh}}$ ) increases (in the absolute value) with an increase in the film thickness and approaches the value of  $-2.55$  eV for the C(100) films and  $-2.0$  eV for the C(111) films. However, the stability of the film-substrate systems characterized by  $E_{\text{sep}}$  is not so simple thing. Fig. 4 demonstrates that the diamond layers thicker than 8 ML are not stable on Cu(100) substrate ( $E_{\text{sep}} > 0$ ). In other words, thick diamond films cannot grow on Cu(100) surface. On the another hand, the films formed on the Cu(111) surface have a tendency to be stable when their thickness becomes larger than 9 monolayers ( $E_{\text{sep}} < 0$ ). It must be noted that a very thin carbon film on Cu(100) surface (of two monolayers) is also unstable. These results correlate with experimental data [7–9] showing that diamond microcrystallites grown on the copper polycrystalline substrates have the (111) orientation mainly.

In order to be sure that results obtained for the only  $k$ -point in the Brillouin zone are correct, I have carried out test calculations using nine  $k$ -points ( $3 \times 3 \times 1$  scheme). In particular, I recalculated the epitaxy of diamond on the Cu(100) surface for two-, four- and six-atomic-layer films. Geometry parameters (bond distances and bond-bond angles) were found to be very similar to those for the one-point case (mismatches are of about 1%). Energy parameters (cohesion, adhesion and separation energies) are collected in Table 3. One can see that they differ from one-point values by 0.1–0.3 eV and keep the general laws inherent in the previous calculations. Thus, it is possible to conclude that the common results of the above one  $k$ -point simulations are rather correct and display the real laws of the diamond epitaxy on copper.

Table 3

Comparison of cohesion (mean), adhesion and separation energies for the diamond epitaxy on Cu(100) calculated using one and nine  $k$ -point schemes

The number of carbon atomic layers	2		4		6	
	1	9	1	9	1	9
$E_{\text{coh(mean)}}$	7.15	7.33	7.28	7.45	8.02	8.21
$E_{\text{adh}}$	-1.84	-1.97	-2.40	-2.49	-2.49	-2.67
$E_{\text{sep}}$	1.53	1.35	-2.31	-2.41	-1.63	-1.70

#### 4. Summary

Ab initio calculations show that epitaxial diamond films can be grown on copper substrates with geometry parameters similar to those of bulk diamond. The mean cohesive energy for the C(100) films are larger than that for the C(111) films; however, the C(111) films are more stable against the separation from the copper substrate. The latter fact explains why the preferable observed orientation of diamond microcrystallites on copper is the  $\langle 111 \rangle$  one.

Certainly, this work is only a first attempt to study theoretically such complicate problem as the diamond epitaxy on metals is. I did not consider other directions of diamond crystal growth (besides of (100) and (111)) and the effects of surface steps. Possibility of carbon clusters to be initial precursors of diamond growth was not studied too as well as many other aspects of the problem. This is an interesting field for future investigations.

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