First-principles calculation study on the stabilities of the (100) and (111) surfaces of boron-doped diamond

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ABSTRACT

Boron-doped diamond (BDD) has attracted much attentions in semi-/super-conductor physics and electrochemistry, where the surface structures play crucial roles. Herein, we systematically re-examined the probable surface reconstructions of the bare and H-terminated BDD(100) and (111)
surfaces by using density functional theory (DFT). For the optimized structures, we performed STM image simulations based on Tersoff-Hamman scheme and calculations of the projected density of states. We found that: on the BDD(100), the p(2x1) reconstruction has lowest energy and the c(2x2) reconstruction has 0.1673 eV/surface-atom energy higher; On the BDD(111), the ideal (1x1) has lowest energy, the single chain SC-(2x1) and Pandey chain PC-(2x1) have 0.3415 eV/surface-atom and 0.6576 eV/surface-atom higher energy, respectively. The BDD(111) appears to have more reconstructions than the BDD(100) which supports to the idea that the BDD(111) is more electrochemically reactive than the BDD(100). In addition, we study the impact of the Boron dopant on the surface states of the BDD(111) and suggest the Boron-enhanced graphitization on the BDD(111). The results give an insight into the surface stability of the BDD.

1. Introduction

Nowadays, diamond is becoming a promising material for a wide range of applications from superconductor [1-3] to electrodes in battery [4-10]. Many chemical activities of diamond-based materials exhibit on the surface [5, 8]. The superconductivity of heavily Boron-doped diamond (BDD) was discussed to be either bulk, type II superconductor [1, 2] or, recently, attributed to the surface Yu-Shiba-Rusinov bands [3]. The ingredient which makes diamond exhibit various properties on the surface is doping. However, the stability of the BDD reconstructions as well as surface electronic properties is still unclear. That is due to the technical difficulties of high-resolution surface measurements as well as the various possible reconstructions of the diamond surfaces depending on the doping conditions during the fabrication process [5, 6, 11-23].

Many theoretical studies proposed various reconstructions of the diamond surfaces [24-45]. On the BDD(100), the (100)-p(2x1) was predicted as the most stable reconstruction [27, 28, 31, 35, 38]; In addition, Song.H proposed dihydride configurations on the diamond (100) and concluded
that the canted/titled (100)-(1x1):2H dihydride phase is the lowest energy among the dihydride structures [34]. On the BDD(111), three reconstructions were widely accepted: ideal (111)-(1x1), single chain (111)-(2x1)-SC, and Pandey chain (111)-(2x1)-PC [38-45]. In additions, both monohydride and dihydride terminations on the (111) surfaces were discussed as possible reconstructions [39, 40]. However, a comprehensive comparison of these reconstructions is still missing and the surface reconstruction energetics is remaining an open question. Moreover, the impact of Boron on the stability and the graphitization of the BDD(111) are in the debate [46].

In this paper, we classify the reconstruction stability (energy comparison) and electronic properties near the Fermi level of the diamond (100) and (111) surfaces with the bare, monohydride and dihydride terminations using first-principles geometry optimizations. The Tersoff-Hamann STM images are then simulated in order to provide the atomistic pictures for the comparison with the STM measurements in the future. Finally, we study the impact of Boron on the surface states of the BDD(111) by analyzing the energy, projected density of states and electron charge density.

2. Calculation methods

To obtain low-energy reconstructions of the surfaces, we use GGA DFT using the PBE [47] exchange-correlation functional implemented in the CPMD package [48]. The normconserving Goedecker pseudopotential [49] is used with 90 Ry cutoff energy. We apply 2x2x1 Monkhorst-Pack K-mesh to all supercells during the geometry optimizations. The systems are optimized by the GDIIS algorithm [50, 51] with the convergence orbital of 1.0x10-5 a.u. and convergence geometry of 2.0x10-3 a.u. All calculations are spin-polarized because of the presence of Boron.

After geometry optimizations, we carry out post-SCF calculations with 6x6x1 K-mesh to obtain total energy and DOS. In particular, we use PAW-PBE exchange-correlation with 400 eV
cutoff energy implemented in VASP package [52-55]. Supercells with 144 and 128 Carbon atoms are used to model the (100) (dimension: 10.107 Å x 5.03 Å x 50.28 Å) and (111) surfaces (dimension: 8.77 Å x 5.06 Å x 50.28 Å), respectively. The Z-axis is chosen to be about three times the thickness of the diamond slabs. Boron doping was represented by one boron dopant atom per 144 (128) carbon atoms (~0.7%). We terminate Hydrogen atoms to all bottom surfaces of the slabs.

The surface energy $E_s$ is defined as:

$$E_s = \frac{E_{\text{tot}} - \sum \mu_i n_i}{N}$$

Where $E_{\text{tot}}$ is total energy of the slab, $\mu_i$ is chemical potential of the boron, carbon and hydrogen, $n_i$ is the number of atoms, and $N$ is the number of the topmost surface atoms of the slab. For the bare and monohydride surfaces, the number of surface atoms is 8 while that number for the dihydride surfaces is 16. The chemical potential of the Carbon, Hydrogen and Boron are -9.09 eV, -3.34 eV, and -5.40 eV, respectively. We consider bulk diamond, isolated H$_2$ molecule, and neutral Boron atom at a lattice site of a bulk diamond to calculate the chemical potentials.

We apply the Tersoff-Hamman approximation [56] to simulate the STM images. The tunneling current is approximated according to the Fermi-Golden rule:

$$I \approx \int_{E_F}^{E_s + eV} \left| M_n \right|^2 N_t(E - eV)N_s(E)dE$$

Where $V$ is bias voltage, $M_n$ is the matrix element, $N_t$ and $N_s$ are the density of states of the tip and surface, respectively. Tersoff and Hamman considered $N_t$ to be constant and the tip’s wavefunction is atomic s-wave-function. The tunneling current, then, becomes:

$$I \propto VN_t(E_F)\sum_s |\Psi_s|^2 \delta(E_s - E_F)$$
The Tersoff-Hamman STM image, thus, reflects the electron density on the surface of the sample.

3. Results and Discussion

3.1. Surface reconstructions of the diamond (100) and (111):

Figure 1 shows the atomistic views of the reconstructed diamond (100) (a) and (111) (b) surfaces. We found two symmetries on the (100): (100)-p(2x1) and (100)-c(2x2). The lower panels show the reconstructions with the presences of H-terminations (monohydride and dihydride). The dimer length of the bare and monohydride (100)-p(2x1) surface are 1.37 Å and 1.62 Å, respectively. While the dimer length of the bare and monohydride (100)-c(2x2) are 1.39 Å and 1.68 Å, respectively. The geometrical difference between p(2x1) and c(2x2) symmetry is that an upper C-C dimer line is right shifted by one primitive cell. Moreover, we found a titled dihydride reconstruction (100)-titled:2H with the dimer length enlarges to 2.52 Å. This dihydride diamond surfaces is identical to canted/titled dihydride surface proposed by Song. H [34]. The differences in dimer lengths among different reconstructions may be a hint to identify the reconstructions in the STM experiment.

We compare the surface energy of the optimized structures in Table. 1. It is shown that the surface energy of the monohydride (100)-p(2x1):1H is the lowest while the (100)-c(2x2):1H surface is 0.1673 eV/surface-atom higher). The dihydride (100)-titled:2H has higher energy than the lowest one about 0.0619 eV/surface-atom. It is noted that the number of surface Hydrogen atoms on the top in a dihydride supercell is 16 while that number in monohydride case is 8. We calculate the chemical potential of Hydrogen from an isolated $H_2$ molecule for all structures. This chemical potential should be different for monohydride and dihydride because of various
conditions in experiment to terminate a dangling bond by either one or two Hydrogen atoms. Nevertheless, our result indicates that there is a high possibility of finding either the monohydride (100)-c(2x2):1H or the dihydride (100)-titled:2H structure in experiment. All the bare surfaces have significantly higher energy than the corresponding monohydride surfaces about 2 eV/surface-atom.

In Fig. 1(b), we show the reconstructed (111) surfaces. All the optimized (111) surfaces were reported in previous DFT papers [38-45]. They are monohydride ideal (111)-(1x1):1H, monohydride single chain (111)-(2x1)-SG:1H, monohydride Pandey chain (111)-(2x1)-PC:1H, and the dihydride single chain (111)-(2x1)-SC:2H. The dihydride Pandey chain is not stable during geometry optimization. The dimer lengths of the bare and monohydride (111)-(1x1) are 1.48 Å and 1.54 Å, respectively. For the Pandey chain, the dimer lengths of the top chain are 1.44 Å (bare) and 1.57 Å (monohydride); the dimer lengths of the lower chain are 1.56 Å (bare) and 1.60 Å (monohydride). For the single chain, the dimer lengths are 1.46 Å, 1.54 Å, and 1.52 Å for the bare, monohydride, and dihydride structure, respectively.

For the diamond (111), the lowest-energy structure is monohydride ideal (111)-(1x1):1H. The monohydride Pandey chain (111)-(2x1)-PC:1H has 0.6576 eV/surface-atom higher than the ideal (1x1). The monohydride single chain (111)-(2x1)-SC:1H has higher surface energy than the ideal one about 0.3415 eV/surface-atom. The bare (111)-(2x1)-PC:0H is 1.5675 eV/surface-atom higher. The bare (111)-(2x1)-SC:0H and bare (111)-(1x1):0H are significant higher in energy about 2.8136 and 2.3210 eV/surface-atom, respectively. We suggest these bare surfaces are not stable. For the dihydride (111)-(2x1)-SC:2H, although it has 1.1211 eV/surface-atom higher energy than the ideal monohydride, there is a possibility that that configuration may survive under extreme conditions. Moreover, the surface energies of monohydride (111) are negative which
mean the reactivity of monohydride (111) is the strongest among all surfaces in this study. The
detail of surface energies is in Table 2.

Table 1. Calculated surface energies of the bare, monohydride, and dihydride BDD (100) surfaces

| Surfaces          | $E_s$ (eV) |
|-------------------|------------|
| (100)-p(2x1):0H   | 2.9104     |
| (100)-p(2x1):1H   | **0.9733** |
| (100)-c(2x2):0H   | 3.0153     |
| (100)-c(2x2):1H   | 1.1406     |
| (100)-titled:2H   | 1.0352     |
Figure 1. The atomistic reconstructions of (a) the diamond (100) and (b) (111) surfaces with bare, monohydride and dihydride terminations. The surface C-atoms are colored by black while the others are brown. The H-atoms are white balls.
Table 2. Calculated surface energies of the bare, monohydride, and dihydride BDD(111) surfaces

| Surfaces           | $E_s$ (eV) |
|--------------------|------------|
| (111)-(1x1):0H    | 1.5314     |
| (111)-(1x1):1H    | -0.7896    |
| (111)-(2x1)-SC:0H | 2.0240     |
| (111)-(2x1)-SC:1H | -0.4481    |
| (111)-(2x1)-SC:2H | 0.3315     |
| (111)-(2x1)-PC:0H | 0.7774     |
| (111)-(2x1)-PC:1H | -0.1320    |

3.2. The projected density of states

Figure 2 shows the projected density of states (PDOS) calculated for the (a) diamond (100) and (b) diamond (111) surfaces. We consider all Carbon atoms which stays within 5 Å below the topmost atom as surface Carbon atoms. In figure 2, we show the summations of projected density of states on these surface Carbon atoms decomposed into $s$-, $p$- and $d$-orbital. The PDOS show the dominant contribution of the $p$-orbital in the surface Carbon atoms to the surface-states as well as other states in valence and conduction band. We can see from Figure 2 that there are surface states in the bandgap of the bare structures while there are virtually no surface states in the H-terminated structures. For the (100) surfaces, the bandgap is around 2 eV for monohydride (100)-p(2x1):1H and (100)-c(2x2):1H. The dihydride (100)-titled:2H structure has lower bandgap which is about 1.8 eV. The PDOS of the (111) surfaces are shown in Figure 2(b). We again observe the surface-states staying in the bandgap in the bare structures. Although we observe the surface states in both
bare (100) and bare (111) surfaces, the surface energies of these surface are about 2-3 eV/surface-atom higher in energy than the monohydride case. We suggest that the surface states if they survive in experiment should be found in another surface configurations. For the monohydride surfaces, the surface-states virtually disappear and the bandgaps are 2~2.5 eV. The bandgap for the dihydride (111)-(2x1)-SC:2H is about 2.2 eV. In general, dihydride termination decreases the bandgap to about 10% compared to the monohydride termination.

Table 3. Calculated surface energies of the hybrid graphene/diamond structure (111)-(1x1)-gr:0H, bare (111)-(1x1):0H and monohydride (111)-(1x1):1H with various Boron positions

| Surfaces          | $E_s$ (eV/surface-atom) (111)-(1x1)-gr:0H | $E_s$ (eV/surface-atom) (111)-(1x1):0H | $E_s$ (eV/surface-atom) (111)-(1x1):1H |
|-------------------|------------------------------------------|---------------------------------------|---------------------------------------|
| undoped           | 1.0752                                   | 1.5314                                | -0.7896                               |
| B at 1st layer    | 0.7494                                   | 1.1837                                | -0.7733                               |
| B at 2nd layer    | 0.8399                                   | 1.2950                                | -0.7965                               |
| B at 3rd layer    | 0.7582                                   | 1.1812                                | -0.7906                               |
| B at 4th layer    | 0.7474                                   | 1.3174                                | -0.7994                               |
| B at 5th layer    | 0.8478                                   | 1.2967                                | -0.7984                               |
| B at 6th layer    | 0.9590                                   | 1.3479                                | -0.8000                               |
| B at 7th layer    | 0.9848                                   | 1.3978                                | -0.7998                               |
Figure 2. The projected density of states (PDOS) for the (a) (100) and (b) (111) surfaces. The total DOS is plotted with $s$-, $p$-, $d$-revolved orbital PDOS of the surface Carbon atoms.
3.3. The STM simulation

To simulate the STM images of these surfaces, we apply the Tersoff-Hamann approximation \( \) to estimate the local charge density within the [-1.5:0] eV energy window which corresponds to -1.5 V bias. Figure 3 shows the simulated STM images in the constant height mode of (a) the H-terminated (100) and (b) (111) surfaces. The inset panels are electron charge distributions for eye-guide. For the (100)-p(2x1):1H, the spots have circle shapes which connect to each other in parallel lines. For the (100)-c(2x2):1H, the circle spots connect to each other in a zigzag shape. For the (100)-tilted:2H, the spots are isolated to each other which is similar to the unreconstructed surface and the positions of the spots are not aligned but tilted. The distances between two spots in the (100) STM images are the dimer lengths which are mentioned in previous section. In Fig.3(b), we show the STM images of the H-terminated (111) surfaces. The distances between two spots in the (111) STM images are indicated in Figure 3(b) for convenient comparisons with the STM measurement in the future. For the (111)-(1x1):1H, the spots have triangle shapes with 2.53 Å separations. For the (111)-(2x1)-PC:1H, the spots have oval shapes with rectangular arrangement. The size of the rectangular is 1.26 Å * 4.39 Å. For the (111)-(2x1)-SC:1H and (111)-(2x1)-SC:2H, the size of the rectangular is 2.53 Å * 4.39 Å. The details of the STM morphology in our experiment and simulation can be found in our experiment paper and previous reports of other groups [57-68].
Figure 3. Simulated STM images of various reconstructions on (a) the H-terminated diamond (100), (b) (111) surfaces. Insets show the electron charge density distributions.
Figure 4. Density of states of undoped and B-doped hybrid graphene/diamond (111)-(1x1)-gr:0H surfaces. The position of Boron is changed from 1 to 7.
Figure 5. Density of states of undoped and B-doped diamond bare (111)-(1x1):0H surface. The position of Boron is changed from 1 to 7.
3.4. The impact of Boron on the surface states of the BDD(111)

In this section, we investigate the dependence of surface structures and surface states on the location of Boron dopant. For the H-terminated surface, there is no surface states and the PDOS also does not depend on the Boron’s position. The Fermi level always stays at the top of valence band regardless the Boron’s position. The surface energy is only varied between very narrow energy (-0.77~-0.80 eV) as indicated in Table 3. Therefore, we suspect that Boron only affects on the bare surface and then may enhance the graphitization.

In this paper, we focus on the two surfaces which strongly depend on the Boron’s position: the bare (111)-(1x1):0H and the hybrid graphene-diamond (111)-(1x1)-gr:0H. The reason we study these structures is that there are theoretical and experimental reports [69-77] mention that the hybrid graphene-diamond structure or sp2-on-sp3 carbon-on-carbon structure was observed after CVD processes. The role of Boron was discussed to enhance the graphitization on the diamond (111) surface [46, 69-77] but the mechanism is still unclear. Herein, we compare the two surfaces: bare (111)-(1x1):0H and hybrid graphene-on-diamond (111)-(1x1)-gr:0H in order to identify the role of Boron on the graphitization. Figure 4 and Figure 5 show the PDOS of undoped and Boron-doped of the two surfaces with the variation of Boron’s position. We observe the surface-states remain in the two kind of surfaces but the position of the Fermi level significantly changes from the middle gap to the valence band maximum (VBM) when the Boron moves from the top downward the diamond crystals. For the hybrid graphene/diamond surface in Figure 4, as the Boron is at the layer 1~5, the Fermi level stays near the middle gap and the PDOS strongly depend on whether Boron stays at the odd layer or even layer which is consistent with previous report [46]. We consider these Borons as surface Borons. When Boron stays at the layer 6-7, the Fermi level is very close to the VBM. We consider the Boron at layer 6-7 as bulk Boron. The surface
states still remain regardless the Boron’s position. The situation is repeated in the bare (111)-(1x1):0H surface (Figure 5). The Fermi level stays very near VBM when Boron is at layer 7. We consider Boron at layer 7 as bulk Boron in this case. Interestingly, a clear bandgap appears when Boron at layer 7 because of the pinning effect. All the surface states are pinned to the E_F near the VBM due to the bulk Boron and leaving a clear bandgap as can be seen in Figure 5. This finding provides an indication to detect the graphene-on-diamond structure based on the position of surface states.

In our simulation, we cannot get the hybrid graphene-on-diamond (111)-(1x1)-gr:0H structure directly from the optimization of the bare (111)-(1x1):0H. To study the impact of Boron on the formations of the surfaces, we calculate the surface energy in Table 3. In Table 3, we report the surface energy of undoped and B-doped structures: hybrid graphene-on-diamond (111)-(1x1)-gr:0H, bare (111)-(1x1):0H and monohydride (111)-(1x1):1H. The impact of Boron on the unterminated surfaces is clear: the surface energy significantly decreases with the presence of Boron in the (111)-(1x1)-gr:0H and bare (111)-(1x1):0H while there is virtually no change in the monohydride (111)-(1x1):1H. Moreover, in the two unterminated surfaces (111)-(1x1)-gr:0H and the bare (111)-(1x1):0H, the surface energy increases from surface Boron to bulk Boron which means Boron prefers to stay near the bare surface rather than in bulk. Although our slab has only 16 Carbon layers, this result supports the idea that Boron can stabilize the bare surface of BDD(111) and that the graphene-on-diamond structure can be formed.

To clarify the mechanism how the surface Boron stabilize the bare (111)-(1x1):0H as well as why the PDOS significantly depends on whether the Boron stays in the odd or even layer, we analyze the spatial distribution of the charge density. Figure 6(a) shows the charge density of the bare undoped (111)-(1x1):0H in front and side views. The difference in colors is for eye-guide only in
order to easily distinguish different layers. The charge density can be divided into three regions namely: sp2, sp2.5, and sp3. In the region sp2, the charge density at individual Carbon atom has p-like shape and connects to the neighbors in 2D dimension. In the region sp3, the charge density at individual Carbon atom has tetrahedral shape and connects to the neighbors in 3D dimension. In the transition region sp2.5, there are two kinds of Carbon atoms: p-like Carbon and sp3-like Carbon. The p-like Carbon is similar to the Carbon in sp2 region, the sp3-like Carbon is similar to the Carbon in the sp3 region. The charge density at the sp3-like Carbon has tetrahedral shape but it does not connect to the lower neighbors along the vertical direction. Figure 6(b) illustrates the arrangement of p-like and sp3-like Carbons of the sp2.5 region in the diamond matrix. The p-like Carbon occupies the top conner of a tetrahedral while the three sp3-like Carbons occupy the three lower conners of a tetrahedral as shown in Figure 6(b). This arrangement creates odd and even layers which reflect the difference in PDOS of Boron atom and the fluctuation of the surface energy as Boron move from the odd layer to the even layer as well [46]. The mechanism why Boron can stabilize the bare (111) surface is proposed in Figure 7. It can be seen from Figure 7 that regardless Boron stays at either even or odd layer, it always creates a bond with either Carbon atom in the lower layer or Carbon atom in the upper layer, respectively. This mechanism stabilizes the sp2.5 region. This mechanism also explains why the structure can be stabilized even though there are many dangling bonds remains on the top as shown in Figure 5.
Figure 6. The atomic view of the surface structure of the diamond (111)
4. Conclusions

We systematically investigate the various low-energy reconstructions of the diamond (100) and (111) surfaces using density functionals theory. For the (100), we found three low-energy reconstructions: two monohydride surfaces: (100)-p(2x1):1H, (100)-c(2x2):1H, and one dihydride surface: (100)-titled:2H; The monohydride structures are the most stable ones, the dihydride structure is about 0.0619 eV/surface-atom higher in energy than the lowest one. For the diamond
(111) surfaces, there are four low-energy reconstructions: three monohydride surfaces: (111)-(1x1)-1H, (111)-(2x1)-PC:1H, (111)-(2x1)-SC:1H and one dihydride surface: (111)-(2x1)-SC:2H. The monohydride structures are the most stable ones, the dihydride structure is about 1.1211 eV/surface-atom higher in energy than the lowest. These results indicate the high stability of monohydride surfaces which should be observed in experiment. Moreover, the dihydride structures may survive under extreme conditions. The STM images are simulated for the further consideration in the STM measurement in the future. Finally, we study the impact of Boron near the (111) surface. We categorize three regions near the bare diamond surface (111) namely sp2, sp2.5 and sp3 regions. The atomic structure of the region sp2.5 allows us to explain how Boron can stabilize the bare diamond surface (111). The formation of the graphene-on-diamond structure thus can be enhanced with the presence of surface Boron.

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