

Origin of Growth Direction Selectivity in CVD of h-BN/Graphene Heterostructure

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Abstract

To elucidate the origin of growth direction selectivity in chemical vapor deposition of hBN/graphene heterostructure, C atom adsorption on Cu(111) surface partially covered with hBN or graphene nanoribbon is studied by using the first-principles method with van der Waals correction. It is found that C atom can attach to the bare edge of hBN nanoribbon, while it does not attach to the H-terminated N-edge. It is also found that the C atom cannot position underneath the nanoribbons. These results suggest that the H-edge-termination controls the growth direction of hBN/graphene heterostructure.

1. Introduction

The heterostructures of two-dimensional materials, graphene and h-BN, give us new opportunities for electronic applications. Recently, we have successfully controlled to form both vertical and lateral hBN/graphene heterostructures by chemical vapor deposition (CVD) growth [1]. We used Cu substrate, and formed monolayer graphene by introducing C source first. Next we formed monolayer hBN laterally connecting to the graphene by introducing BN source, and then formed monolayer graphene under the hBN by introducing C source, again. Thus, we formed vertical hBN/graphene heterostructure as well as lateral heterostructure. We have also proposed that the origin of growth direction selectivity is H termination of edges theoretically [2].

In this contribution, we further study the origin of growth direction selectivity theoretically. We study C atom adsorption on Cu(111) surface partially covered with hBN or graphene nanoribbon by using the first-principles method with van der Waals correction. We found that whether the edge is terminated by H or not surely relates to the growth direction of graphene.

2. Calculation method

We perform the first-principles calculation based on the density functional theory with the program package of PHASE/0 [3]. We employ the PAW method with the cutoff energy of 30 Ry. The $2 \times 4 \times 1$ Monkhorst-Pack grid is used for the k-point sampling.

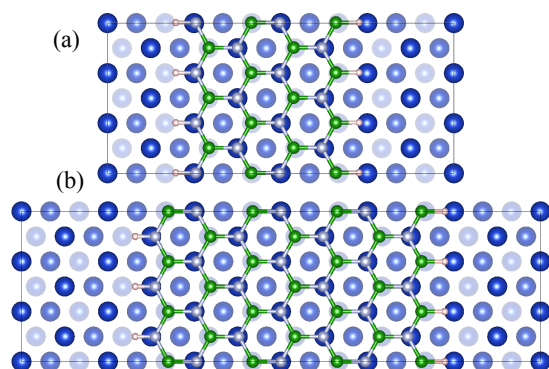


Figure 1 Atomic structure top views of calculated unit cell covered with hBNNR (a) for $3 \times 4\sqrt{3}$ and (b) $3 \times 6\sqrt{3}$ cells. Blue, orange, white, and green spheres represent Cu, H, N, and B atoms, respectively.

Because the graphene or hBN sheet is adsorbed on the Cu surface by the van der Waals interaction, we must take into account the van der Waals correction. It is widely known that the selection of correction method affects the calculated results. In this study, we focus on the SCF vdW-DF1 method as the correction [4]. As our previous study, we suppose that the SCF vdW-DF1 method does not affect the overall discussion in this work [2].

We employ the repeated slab geometry with four Cu atomic layers, one graphene or hBN layer, and a vacuum region with the thickness of about 9.72 Å. The $3 \times 4\sqrt{3}$ and $3 \times 6\sqrt{3}$ supercell of Cu(111) is used. The surfaces are covered with the $3 \times 2\sqrt{3}$ and $3 \times 3\sqrt{3}$ supercell of graphene or hBN zigzag nanoribbon, respectively, which is appropriately expanded to match the lattice periodicity to that of Cu(111). Therefore, the graphene nanoribbon (GNR) and hBN nanoribbon (hBNNR) are expanded by 4.09 % and 2.33 %, respectively, in the direction parallel to edges. We put GNR and hBNNR so that B or C atom positions on H3 site, and N or C atom on T1 site according to our previous study [2]. The atomic models are shown in Fig. 1. For the GNR model, we have two different orientation edges. For one edge, the edge C atom positions on T1 site. For the other edge, it positions on H3 site. We hereafter call the former edge as T1 edge and the other as H3 edge. We fully optimize the atomic positions except for all outermost Cu atoms at the bottom surface to evaluate the formation energies.

3. Results and discussion

First, we calculate initial structures covered only with nanoribbons. The optimized results for the $3 \times 6\sqrt{3}$ structure with hBNNR are shown in Fig. 2. The results are similar to our previous results for the $3 \times 4\sqrt{3}$ structure with narrower hBNNR [2]. hBNNR and GNR with H-terminated edges position horizontally on the surface, while those with bare edges are curved and terminated by the Cu surface. Therefore, we can conclude that the nanoribbon shapes are independent of the ribbon width. The GNR shape dependence on the edge termination is consistent with previous theoretical reports [5,6].

Next we put a C atom close to the bare edges, and examine its connection to the nanoribbon by using the $3 \times 4\sqrt{3}$ structure. The optimized results are shown in Fig. 3(a) and (b). The energy gains relative to the H3 site at center of bare surface area are 0.61 eV, 0.69 eV, 0.67 eV, and 1.08 eV for GNR T1, GNR H3, hBNNR N and hBNNR B edges, respectively. These indicate that the GNR

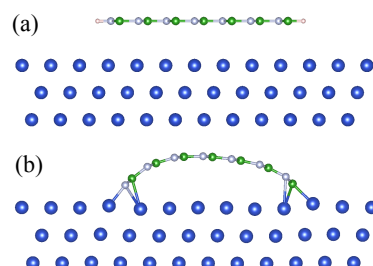


Figure 2 Atomic structure side views of optimized results for hBNNR $3 \times 6\sqrt{3}$ structure with (a) H-terminated edge and (b) bare edge.

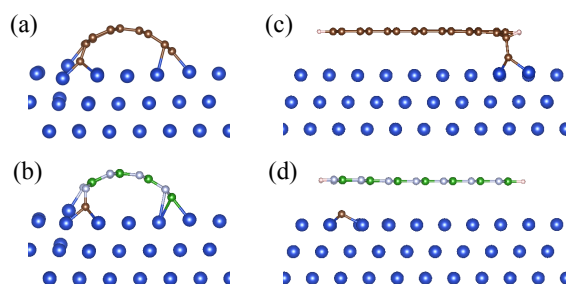


Figure 3 Atomic structure side views of optimized results for C adsorbed to (a) GNR bare edge, (b) hBNNR bare edge, (c) GNR H-terminated H3 edge, and (d) hBNNR H-terminated N edge. Brown spheres represent C atoms.

H3 edge is more reactive than the T1 edge. These also indicate that the hBNNR B edge is more reactive than the N edge. Even though the adsorption energy of subsurface site is more stable by about 0.34 eV than H3 site, it is clearly suggested that graphene can grow from the bare edges of both GNR and hBNNR. This must promote lateral hBN/graphene heterostructure formation as well as lateral graphene growth. Our results for GNR are consistent with the previous theoretical report, while the previous report did not comment on the edge orientation dependence [5].

Then we put a C atom close to the H-terminated edges, and examine its connection to the nanoribbon by using the $3 \times 4\sqrt{3}$ and $3 \times 6\sqrt{3}$ structures. The optimized results for the $3 \times 6\sqrt{3}$ structure are shown in Fig. 3(c) and (d). The energy gains for the $3 \times 4\sqrt{3}$ structure relative to the center of bare surface area are -0.33 eV, 0.88 eV, -0.36 eV, and 0.15 eV for GNR T1, GNR H3, hBNNR N and hBNNR B edges, respectively. Those for the $3 \times 6\sqrt{3}$ structure are -0.19 eV, 0.92 eV, -0.16 eV, and 0.23 eV. These clearly indicate that C atom cannot connect to GNR T1 and hBNNR N edges as we expected. However, these also clearly indicate that C atom can connect to the other edges such as GNR H3 edge, even if we take into account the more stable subsurface site. As shown in Fig. 3(c), the additional C atom have a bond with the H3 edge C atom. It is suggested that graphene cannot grow from the H-terminated GNR T1 and hBNNR N edges, while that can grow from the H-terminated GNR H3 edge. Since the shape of hBN islands is the triangle with N edges according to our previous experimental study [1], this must prohibit the lateral hBN/graphene heterostructure formation. However, since the shape of graphene islands is the hexagon with both zigzag edges, this might promote lateral graphene growth even when the edges are terminated by H. C connection to the H-terminated GNR edge was not reported in the previous theoretical study [5].

Finally, we put a C atom at various positions such as H3 and T4 sites on the Cu surface including the positions underneath nanoribbon, and calculate the adsorption energy for the $3 \times 6\sqrt{3}$ structure. The calculated results are summarized in Fig. 4. The standard of relative adsorption energy is the H3 site at center of bare surface area. This indicates that the positions underneath nanoribbon (position 3-8) are less stable than bare surface area (position 0-2 and 10-12) both for hBNNR and GNR. The exceptions are only the positions around hBNNR B and GNR H3 edges (position 9), where C atom might connect to the ribbon edge. It is suggested that graphene cannot nucleate under H-terminated hBN or graphene islands, but can nucleate on bare surface areas, which are not covered with any hBN or graphene islands. The growing graphene on bare surface area could penetrate under the H-terminated hBN or graphene island and form vertical hBN/graphene heterostructure or bilayer graphene, because the edge of growing graphene might be rather terminated by surface Cu atoms. The lower adsorption

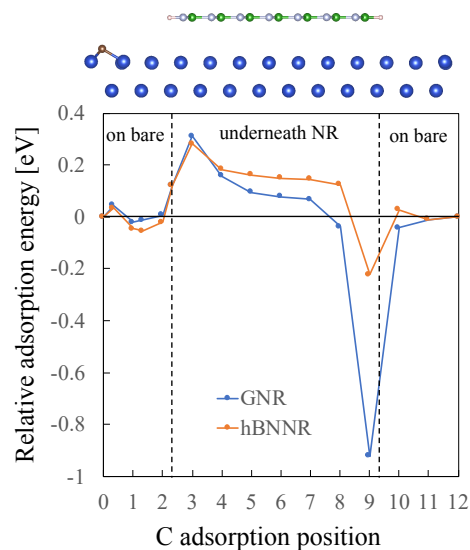


Figure 4 Relative adsorption energy of a C atom as the function of adsorption position for the surfaces partially covered with H-terminated GNR or hBNNR.

energies near the H-terminated N edge (position 1-2) seems consistent with experimental results, which indicates graphene tends to nucleate at the edges of hBN islands [7].

From the above results, we can confirm that the H edge termination is the key factor for the control of growth direction of hBN/graphene heterostructure. If the edge is not terminated by H, the graphene grows from the edge of hBN island, and lateral heterostructure can be realized. If the edge is terminated by H, the graphene cannot grow from the edge of hBN island, and penetration of graphene under the hBN island realize the vertical heterostructure. Such H edge termination effect is rather unique for hBN island, and the effect for graphene island is not so clear and more complicated.

4. Conclusions

We study C atom adsorption on Cu(111) surface partially covered with hBN or graphene nanoribbon by using the first-principles method with van der Waals correction. We find that graphene can grow from bare edge of nanoribbons. We also find that the graphene cannot grow from H terminated hBN N or GNR T1 edge, but can grow from H terminated GNR H3 edge. Because the shape of hBN islands in CVD growth is triangle with N edges, these results suggest that H edge termination controls the growth direction of hBN/graphene heterostructure.

Acknowledgment

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