First-principles study of the surface structure and stability of BC$_5$

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Abstract

BC$_5$ with both superhard and superconducting properties is expected to have important applications in many fields. In this work, the low-index surface structures and properties of BC$_5$ have been identified by first-principles calculations. The surface stability decreased in the order of (011) > (010) > (101) > (100) > (110) > (111) > (001). The (011), (101), and (110) surfaces exhibit the strongest surface relaxation, followed by (111), and the (001) surface is the least. A DFT (density functional theory)-based Wulff construction of the equilibrium shape of BC$_5$ shows that the surface with the largest exposure area is (011), followed by the (101) and (001) surfaces. Electronic analyses show that Pmma phase BC$_5$ and all considered low-index surfaces exhibit metallic character where the surfaces are even stronger. Larger charge redistribution in the low-index surfaces is found compared with the bulk case.

1. Introduction

Since superhard diamond-like BC$_5$ (d-BC$_5$) was synthesized [1], it has received much attention [2–5] due to its reported high bulk modulus (335 GPa) and thermal stability (as high as 1900 K). It broadened the superhard materials family and can be used in some specific fields where diamond has limits to be applied to, for example, cutting the ferrous metals at high-speed in machining processes. Moreover, different from the diamond, d-BC$_5$ is found to show conductive character [4, 6–11], which can be used in the advanced miniaturization of microelectronic, for example, as the interlayers of copper/diamond composites (typical electronics packaging materials) [12, 13].

The synthesized superhard diamond-like BC$_5$ by Solozhenko et al [1] presents a cubic bulk structure. Using the transmission electron microscopy, they observed cubic-BC$_5$ formed nanocrystalline aggregates after quenching at room temperature [1]. They also proposed that for diamond-like B–C materials, cubic-BC$_5$ represented the metastable limit solubility of boron in diamond (16 at% of B) [1]. Recently, Baker et al [14] synthesized a superhard d-BC$_5$ with a boron-content up to 7.7 at% using the microwave plasma chemical vapor deposition on a silicon substrate. The Scanning Electron Micrograph of the sample (2.9 at% boron) revealed a (100) plane and a further increased boron content to 7.7 at% causes a less faceted structure. They proposed that the most stable bulk BC$_5$ presents an orthorhombic phase with Pmmn symmetry employing evolutionary algorithms combined with DFT [14]. However, due to the lack of important information such as atomic coordinates in experiments, it is necessary to use first-principles calculations to determine the possible stable bulk and surface structures. Many efforts have been devoted to investigate the structure and properties of bulk d-BC$_5$ based on the first-principles calculations. Yao et al [15] used comprehensive structural searches and first-principles structural optimizations to predict a thermodynamically stable I–4m2 phase of superhard BC$_5$. Later, Xi et al [16] claimed that Pmmn was more stable than I–4m2. The same conclusion has been obtained by Li et al [2], Alp et al [3], and Baker et al [14]. Using thorough structural searches with an evolutionary algorithm, Li et al [2] proposed the orthorhombic Pmmn structure was thermodynamically the most favorable among the P3m1.
Imm2, I-4m2, and Pmma phases and agreed well with the experimental x-ray diffraction and Raman data. Alp et al. [3] then explored the candidates to nine possible bulk phases (F-43m, P6/mmm, Cmcm, Pmma, P-1, P3m1, Imm2, I-4m2, and Pmma), and among them, Alp et al. [3] found that simple orthorhombic Pmma was the most stable one based on first-principles calculations. Despite much of the previous theoretical work has focused on the structure and properties of bulk BC₅, research on the surface structures and morphology, which plays an essential part of understanding fundamental physical properties and potential applications, has not been found yet. It has been clearly proved that a DFT-based Wulff construction is a reliable tool for identifying the single crystal shape under equilibrium conditions [17–21]. In the present work, we will explore the surface structures and present the equilibrium crystal shape of BC₅ using Wulff construction.

2. Models and methods

The bulk structure is taken from [3], exhibiting Pmma phase which is determined to be the most stable bulk structure by several groups [2, 3, 22] (figure 1). The (001), (010), (100), (101), (110), and (111) surfaces present six, two, one, three, one, and two terminations (figure 1). Twelve, eight, twelve, eight, twelve, and eight layer thickness is employed for the (001), (010), (100), (101), (110), (011), and (111) surfaces, respectively, and half of them at the bottom are fixed to represent the bulk structure. Note that not every termination configuration is symmetric; therefore, self-consistent dipole correction along z direction is employed. At least 12 Å vacuum layer is added along z direction.

The spin density-functional theory calculations with plane-wave ultra-soft pseudopotential approach [23] and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) functional [24] are performed in CASTEP code [25, 26]. Ultra-fine quality is set for geometry optimization, e.g. energy cutoff is 310 eV; the convergence threshold for the maximum energy change and force is 5.0 × 10⁻⁶ eV/atom and 0.01 eV/Å, respectively. (16 × 16 × 4), (6 × 6 × 1), (1 × 6 × 1), (6 × 1 × 1), (6 × 1 × 1), (1 × 4 × 1), and (4 × 1 × 1) K points are used for the bulk, (001), (010), (100), (011), (101), (110), and (111) surfaces optimization, respectively. All parameters have been checked to be well converged. The relaxed surface free energy γ is calculated as [27, 28]

\[
\gamma = E_{\text{cut}} + E_{\text{relax}} = (E_{\text{slab-relax}} - nE_{\text{bulk}})/2A + (E_{\text{slab-relax}} - E_{\text{slab-unrelax}})/A
\]

(1)

where \(E_{\text{slab-unrelax}}\) and \(E_{\text{slab-relax}}\) are the total energies of the unrelaxed and relaxed slab (half of the slab at the bottom are fixed to represent the bulk structure, namely, only the upper surface relaxed), \(n\) is the number of BC₅ unit in the slab, \(E_{\text{bulk}}\) is the bulk energy per BC₅ unit, and \(A\) is the surface area. For the unrelaxed surface free energy \(\gamma_{\text{unrel}}\), it only includes the first item of equation (1).
Table 1. The calculated unrelaxed and relaxed surface free energies $\gamma_{un}$ and $\gamma_{re}$ (J m$^{-2}$), the unrelaxed and relaxed topest bond length $d_{C-C/B-B}$ (Å), and the surface relaxation degree $\phi$ (%) of BC$_5$ low-index surface structures. To be continued.

| Surf. | (001) $T_0$ | (010) $T_0$ | (100) $T_0$ | (011) $T_0$ | (110) $T_0$ | (111) $T_0$ |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|
| $\gamma_{un}$ | 8.96 | 8.96 | 8.53 | 9.22 | 7.62 | 6.70 | 5.22 | 4.95 | 6.06 |
| $\gamma_{re}$ | 8.57 | 8.25 | 7.09 | 6.71 | 7.49 | 6.01 | 3.75 | 3.85 | 4.02 |
| $d_{C-C/B-B}$ | 1.55/- | 1.56/- | 1.52/- | -1/- | 1.52/1 | -1/1.6 | 1.52/- | 1.53/- | 1.55/1.6 |
| $\gamma_{f}$ | -/4/- | -/4/- | -/4/- | -/4/- | -/4/- | -/4/- | -/4/- | -/4/- | -/4/- |
| $\phi$ | 4.3 | 7.9 | 16.9 | 27.2 | 1.7 | 10.3 | 28.1 | 22.3 | 33.6 |

$^*$ $\phi = (1 - \gamma_{re}/\gamma_{un}) \times 100\%$.

3. Results and discussion

3.1. Bulk structure

The optimized bulk parameters of BC$_5$ with Pmma phase are $a = 2.497$ Å, $b = 2.522$ Å, and $z = 11.460$ Å, respectively, which is close to the previous calculated values [2, 3, 22].

3.2. Surface structure

The surface structure and properties is of great importance for various applications, such as catalysis and growth of nanoparticle [29-32]. For all considered low-index surfaces, we first identify the most stable termination of each surface. As shown in table 1, among six terminations of the (001) surface, the B termination $T_B$ is the most stable with the smallest $\gamma_{re}$ of 6.01 J m$^{-2}$. All surface bonds become shorter compared with the unrelaxed ones indicating the surface bonds contract to the bulk. For the (010) surface, the C/B mixed termination $T_{mix}$ is more stable than the pure C termination by 0.31 eV (30 KJ mol$^{-1}$) lower in energy, however, due to the stronger surface construction of $T_C$, the pure C termination $T_C$ exhibits a smaller $\gamma_{re}$ by 0.10 J m$^{-2}$. Note that for all the others surfaces, the most stable termination with the lowest energy presents the smallest relaxed surface free energy. Compared with the (001) and (010) surfaces, the (100) surface with only one mixed C and B termination $T_{mix}$ is less stable than the (010) surface, but more stable than the (001) surface. Among them, it exhibits the largest surface relaxation degree $\phi$ of 33.6%. The second and third layers B move downwards, forming new B-B bonds (figure 2).

For (101), the most favorable energetically termination is the mixed C and B $T_{mix2}$, where the surface B together with its bonded topest C atoms (in black in figure 2) moved downwards forming a C-B-C-B-C-B six-membered ring with the sub-layer B, resulting in the smallest surface free energy of 3.28 J m$^{-2}$ (table 2). The pure C termination $T_C$ is the least stable with $\gamma_{re}$ of 3.70 J m$^{-2}$. The (110) surface exhibits strong surface reconstruction, where C-C dimers are formed (marked by dash circle in figure 2), yielding the surface relaxation degree $\phi$ as high as 46.5%. The formed C-C dimer yields a bond length of 1.42 Å, while the original C-C distance before relaxation is 2.52 Å. The similar dimer reconstruction phenomenon [33-35] has been observed on the diamond (001), Si(001), and Ge(001) surfaces. Among three terminations of the (011) surfaces, one of the carbon terminations $T_{C1}$ is energetically the most favorable with the strongest surface reconstruction ($\phi = 49.1\%$) and the corresponding relaxed surface free energy is 2.74 J m$^{-2}$, which is the smallest among all considered low-index surface structures. It is noticeable that during the surface reconstruction, a C-C bond...
between the topest C and the sublayer C broke yielding a carbon nanotube. The other C termination T_{C2} and the mixed C and B termination T_{mix} exhibits similar stability with identical γ_{re} of 2.97 J m^{-2} and surface relaxation degree φ of about 44%. Considering the surface relaxation, the (011), (110), and (101) surfaces yield stronger surface relaxation than the (100), (010), and (001) planes. For the (111) surface, the C termination T_{C1} and the B termination T_{B} shows the similar stability with almost the same relaxed surface free energy γ_{re} of ~4.34 J m^{-2}. The corresponding surface relaxation degree is about 40% suggesting the relaxation of these surfaces is strong. The similar result is found in our previous studies where Fe_{4}C surfaces yielded the largest relaxation degree of 39.0% [36].

As shown in tables 1, 2, and figure 2, the surface bonds contract compared with the bulk ones, resulting from the reduced coordination number of the surface atoms. For most cases, the C-C bond length shrinks from ~1.83 Å in the bulk to ~1.44 Å on the surface, and the C-B bond distance changes from ~1.64 Å in the bulk to ~1.48 Å on the surface. The B-B distance contracts from 1.83 Å in the bulk to ~1.68 Å on the surface.

Summarizing, other than the (011) and (111) surfaces, the B-containing termination (T_{B} or T_{mix}) is more stable than the pure C termination. The surface stability decreased in the sequence of (011) > (010) > (101) > (100) > (110) > (111) > (001). In general, the [110] plane exhibits the strongest surface relaxation, followed by the (111), and the [100] plane is the least.

To obtain the equilibrium crystal shapes of BC_{5} including dominant surface orientations and surface anisotropy under equilibrium conditions, a Wulff construction using the DFT predicted surface energies is performed using VESTA software [37–40]. The largest exposed surface is {011} (the containing surfaces please see figure 3, same below) with the largest surface area portion, followed by the [101] and [001] surfaces. The surface area of the {011}, [101], [001], and {110} accounts to about 45%, 37%, 16%, and 2% of the total surface area, respectively.
3.3. Electronic property
To understand the bond nature of bulk and surface structures of Pmma phase BC5 better, we performed calculations of the total and projected density of states (DOS and PDOS). Pmma phase BC5 presents metallic character on the base of the positive DOS values at the Fermi level (figure 4), which is in line with the previous experimental [1] and theoretical results [10]. The major contribution to Fermi level is from the p orbitals of B and C atoms. Another clear trend is observed from the DOS that the surfaces exhibit more metallic character than the bulk according to the increased DOS values at the Fermi level. In particular, the DOS values at the Fermi level of the (001) surface increase dramatically (~7 times of that of bulk) where the surface B orbitals contribute ~1/3. The PDOS (figure 4) and electron density map (figure 5) show that the covalent C–C and B–C bonds both exhibit a strong directionality. According to the electron density map (figure 5), the C–C bonds are stronger than the B–C bonds.

To verify qualitative trends in charge redistribution, we performed Mulliken [41] and Hirshfeld [42] charges analyses. As shown in table 3, stronger charge redistribution in the low-index surfaces is found compared with the bulk case. For most of surfaces, the topest surface B devotes more electrons than bulk B excluding the (110)
and (011) surfaces where the charge of the topest surface B is close to the bulk case. For these two surfaces, the surface C atoms which is bonded to the topest surface B is found to present less negative charges than bulk C suggesting they accept less electrons compared with the bulk case, which may be related to the cleavage of surface C-C bonds.

4. Conclusion

The synthesized diamond-like BC5 is expected to have important applications in the development of high-pressure devices for studying the electrical and superconducting properties of various materials due to their superhard and superconducting properties. In this work, the surface structures (atomic and electronic) and morphology of BC5 have been identified based on first-principles calculations. Except for the (011) and (111) surfaces, the B-containing termination (TB or Tmix) is more stable than the pure C termination (TC). The surface stability decreased in the sequence of (011) > (010) > (100) > (110) > (111) > (001). In general, the {110} plane exhibits the strongest surface relaxation, followed by the (111), and the {100} plane is the least. The surface bonds are found to contract compared with the bulk ones, resulting from the reduced coordination number of the surface atoms.

The Wulff construction of the equilibrium shape of BC5 shows that the surface with the largest exposure area is (011), followed by the (101) and (001) surfaces.

Electronic analyses show that Pmma phase BC5 and all considered low-index surfaces exhibit metallic character where the surfaces are even stronger. Larger charge redistribution in the low-index surfaces is found compared with the bulk case where for most of surfaces excluding the (110) and (011) surfaces, the topest surface B devotes more electrons than bulk B.

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