Unexpected Reconstruction of the \(\alpha\)-Boron (111) Surface

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We report on a novel reconstruction of the \(\alpha\)-boron (111) surface, discovered using an \textit{ab initio} evolution structure search, and reveal that it has an unexpected neat structure and much lower surface energy than the recently proposed (111)-I\(_{R,(a)}\) surface. For this reconstruction, every single interstitial boron atom forms bridges with the unique polar-covalent bonds between neighboring \(B_{12}\) icosahedra, which perfectly meet the electron counting rule and are responsible for the reconstruction-induced metal-semiconductor transition. The peculiar charge transfer between the interstitial atoms and the icosahedra plays an important role in stabilizing the surface.

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The element boron has been attracting an enormous amount of attention owing to its fascinating properties, such as fascinating structural complexity, superhardness, unusual partially ionic bonding, and superconductivity at high pressure [1–5]. As a neighbor for carbon, boron is in many ways an analog of carbon and its nanostructures (clusters, nanotubes, nanowires, nanobelts, fullerenes and so on) have aroused extensive interest, in the hopes (clusters, nanotubes, nanowires, nanobelts, fullerenes and so on) have aroused extensive interest, in the hopes of exploring other likely reconstructions and the stabilization mechanisms by first-principles calculations.

\(\alpha\)-boron structure is composed of \(B_{12}\) icosahedra [28], has two inequivalent atomic sites, polar \((B_p)\) and equatorial \((B_e)\) sites, the \(B_p\) atoms form upper and lower triangles of an icosahedron and the \(B_e\) atoms form a waving hexagon along the equator of an icosahedron [2]. The arrangement of icosahedra in \(\alpha\)-boron can be described as a cubic close packing with the layer sequence ABC [1]. Compared with the (111)-I\(_{R,(a)}\) surface that built along [111] direction of the primitive rhombohedral cell with the surface vectors \(U(2\bar{1}1)\) and \(V(112)\), we cleaved the surface along [111] direction with the surface vectors \(U(\bar{1}12)\) and \(V(110)\), which allowed us to reduce the required computational resource drastically. The calculations were conducted on the 4 layered \(B_{12}\) icosahedra of the (111)-I substrate, and then (111)-II substrate was also tested [25, 26]. In both cases we obtained exactly the same reconstruction, regardless the type of substrate if enough atoms and thickness are used. Structure searches for the reconstructions were performed using the \textit{ab initio} evolutionary algorithm \textit{uspeX} [29–31], which has been successfully applied to various materials [32–34]. The number of surface atoms was allowed to vary from 1 to 20 with the vacuum layer of 10 Å, which are restricted to the surface layer of thickness 4 Å. Given that the thickness of \(B_{12}\) icosahedron is \(\sim3.7\) Å, there is an enough space to fully explore the chemical landscape in our calculations. The all-electron projector-augmented wave method [35] was employed, as implemented in the Vienna \textit{ab initio} simulation package (VASP) [36] with the generalized gradient approximation (GGA) and the functional of Perdew, Burke, and Ernzerhof (PBE) [37]. A plane-wave cutoff energy of 500 eV and a Monkhorst-Pack Bril-
loin zone sampling grid with resolution $2\pi \times 0.04$ Å$^{-1}$ were used. In addition, the hybrid HSE06 functional with the screening parameter ($\omega$) 0.2 Å$^{-1}$ was also employed to check the robustness of surface energies [38].

For the most stable (111)-$I_{R,(a)}$ surface, there is buckling and coupling among three outer atomic layers above the icosahedral $B_{12}$ units, which result in structural complexity [26]. In contrast to (111)-$I_{R,(a)}$, our reconstruction [designated as (111)-$I_{R,(z)}$] has an unexpected neat structure, as shown in Fig. 1(a), where a single boron atom occupies the interstitial position (named as $B_i$, colored in red), connects the $B_i$ atoms (colored in blue) and forms bridges with bond lengths of 1.793 Å and bond angles of 113.06°. The $B_i$ atoms are slightly above the topmost icosahedral atoms ($B_k$), see Fig. 1(b), which form the modulated “3 + 9” membered rings on the topmost surface. Interestingly, the (111)-$I_{R,(z)}$ and (111)-$I_{R,(a)}$ share almost the same surface motif (3 + 9 structure), which hints that the (111)-$I_{R,(a)}$ surface may be a local metastable phase. According to the surface energy $\sigma = (1/2A) (N\epsilon_{bulk} - E_{slab})$, where $A$ denotes the surface area, $\epsilon_{bulk}$ is the energy per atom in the bulk $\alpha$-boron and $E_{slab}$ is the energy of the substrate containing $N$ atoms [26]. We calculate the surface energies of (111)-$I$ and (111)-$I_{R,(a)}$ by using the GGA-PBE and HSE06 methods, as listed in the Table I, which are in excellent agreement with previous results [26]. This establishes the reliability and accuracy of our calculations. Strikingly, the surface energy of (111)-$I_{R,(z)}$ is 128.23 meV/Å$^2$ for GGA-PBE and 136.79 meV/Å$^2$ for HSE06, which is considerably, by 42 and 60 meV/Å$^2$ respectively, lower in energy than the (111)-$I_{R,(a)}$ structure. To confirm the most stable surface, we also perform the structure search with the same substrate proposed by Ref. [26], get the same reconstruction and energy, and find there is no dependence on the choice of the surface vectors/cleavage plane: it is the general rule that the ratio of $B_i$ to the exposed $B_{12}$ icosahedron should be 1 : 1 in $\alpha$-boron (111) surface.

Figure 2 shows the band structures of the unreconstructed (111)-$I$ and the reconstructed (111)-$I_{R,(z)}$ surfaces from the GGA-PBE calculations. Due to the unsaturated dangling bonds, the (111)-$I$ surface is metallic, as shown in Fig. 2(a). In contrast, Figure 2(b) shows the (111)-$I_{R,(z)}$ surface is a semiconductor with a direct DFT band gap of 1.13 eV compared with the band gap of 1.50 eV for bulk $\alpha$-boron. The reconstruction-induced metal-semiconductor transition meets the general principle that reconstructions usually lower their energies by atomic rearrangements leading to semiconducting surface state [27]. According to Wade’s rule [39, 40], a $B_{12}$ icosahedron has 36 valence electrons, 26 of which may be used for intraicosahedral bonds and 10 for intericosahedral bonds. Each icosahedron forms six two-electron-two-center (2e2c) bonds with the icosahedra of neighboring layers, which requires $6 \times 2/2 = 6$ electrons, as well as six closed two-electron-three-center (2e3c) bonds with the neighboring icosahedra in its own layer, these multi-center bonds require $6 \times 2/3 = 4$ electrons [1]. The (111)-$I$ surface cuts three intericosahedral bonds (2e2c) per icos-
hedron, and there are two \( B_{12} \) icosahedra per stacking layer in the \( (111)-I_{R,z} \) surface. Therefore, the unsaturated dangling bonds of the \( (111)-I_{R,z} \) surface need additional \( 3 \times 2 \times 2/2 = 6 \) valence electrons. Two \( B_i \) atoms are just added to the surface, connect six \( B_p \) atoms, as shown in Fig. 1(a), form six bridging B-B bonds (these are the closed 2e2c bonds, may not the same), which perfectly satisfy the electron counting rule (ECR) \([27, 41]\), and are responsible for the reconstruction-induced metal-semiconductor transition.

Projected density of states (PDOS) of the topmost atoms is plotted in Fig. 3. The \( (111)\)-I surface exhibits metallic character, see Fig. 3(a), dominantly due to the out-of-plane states \( (p_z) \) orbitals, arising from the unsaturated \( B_p \) atoms, and located near the bottom of the conduction band. In comparison, strongly hybridized bonding states present in the vicinity of the Fermi level in Fig. 3(b), mainly derive from the \( B_p: p_z \) and \( B_i: p_{xy} \) orbitals, and are fully filled. The \( (111)-I_{R,z} \) surface is thereby a semiconductor. PDOS (Figs. 3c and 3d) clearly shows the out-of-plane \( p_z \) states and the in-plane \( p_{xy} \) states near the valence band edge are dominantly from the \( B_p \) and \( B_i \) atoms, respectively. Because the \( B_i \) atoms are located above empty space, there is no \( p_z \) state for the \( B_i \) under the Fermi level in Fig. 3(d). Moreover, the distance between the \( B_i \) and \( B_e \) atoms is 2.926 Å. All of these facts indicate that there is no interaction/bonding between the \( B_i \) and \( B_e \) atoms, which further confirms the reliability of the surface bonding configuration and the ECR applied for the \( (111)-I_{R,z} \) surface.

Symmetry breaking of \( B_{12} \) icosahedra results in charge asymmetry on some B-B bonds, and in fact a small degree of ionicity of B-B bonds in the \( B_{12} \) icosahedron was predicted in \( \alpha \)-boron \([3]\), while a much greater degree of ionicity was found in the high pressure partially ionic \( \gamma \) phase \([4]\). It is extremely important and interesting to study the charge transfer/ionicity for the \( (111)-I_{R,z} \) surface. Figure 4 shows the charge density difference between \( B_i \) and \( B_p \) atoms \([42]\). There is a notable

![FIG. 2. (Color online) Band structures of (a) (111)-I and (b) (111)-I\(_{R,z}\), the special \( k \) points are labeled as \( \Gamma(0\ 0\ 0) \), \( Y(0\ 0.5\ 0) \), \( S(-0.5\ 0.5\ 0) \), and \( X(-0.5\ 0\ 0) \), respectively.

![FIG. 3. (Color online) [[(a) and (b)] PDOS of the (111)-I and (111)-I\(_{R,z}\) structures. [(c) and (d)]PDOS of the \( B_p \) and \( B_i \) atoms in (111)-I\(_{R,z}\) structure.](image-url)
the charge transfer for these 4 layers should be in the
12-icosahedron comprises 4 atomic layers (labeled from 1 to 4),
contrasted sharply with the intericosahedral purely covalent
transition. In particular, significant charge transfer is re-
ponsible for the unique polar-covalent bonds between
the $B_i$ and $B_p$ atoms. Charge redistribution between the
$B_i$ atoms and the $B_{12}$ icosahedra is one of the key factors
stabilizing the reconstruction.

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FIG. 4. (Color online) (a) Projection of the charge density
difference of the (111)-$I_{R(z)}$ structure along [111] direction.
(b) projection of the charge density difference of the (111)-
$I_{R(z)}$ structure along [112] direction. The top four atomic
layers are labeled from 1 to 4.

charge transfer from $B_i$ to the neighboring $B_{12}$ icosahedra
through $B_p$ atoms. Bader charges for $B_i$ is +0.17$e$,
and +0.04$e$ for $B_p$ [43]. Strikingly, the charge trans-
fer keeps the charge state of $B_p$ close to its bulk state
(∼+0.05$e$)[4, 23], and the significant charge transfer be-
tween the $B_i$ and $B_{12}$ icosahedra indicates the bridging
$B_i$-$B_p$ bonds are unique polar covalent bonds, which
contrasted sharply with the intericosahedral purely covalent
$B_p$-$B_p$ bonds [3]. Due to the charge transfer, the $B_i$-
$B_p$ bonds (1.793 Å) are much weaker and longer than the
$B_p$-$B_p$ bonds (1.673 Å). In Fig. 4(b), each $B_{12}$ icosahedron
comprises 4 atomic layers (labeled from 1 to 4),
the charge transfer for these 4 layers should be in the
“+−−+” order with the values of +0.56, −0.46, −0.46,
and +0.36$e$, compared with the corresponding values of
+0.20, −0.22, −0.22, and +0.24$e$ in α-boron. It is clear
from these numbers that the surface region as a whole
is charge-neutral. The charge transfer of the (111)-$I_{R(z)}$
surface is rebalanced within the top 4 atomic layers (in-
clude the $B_i$ atoms and the $B_{12}$ icosahedra), which plays
an important role in stabilizing the surface.

In conclusion, the most simple and stable reconstruc-
tions of the α-boron (111) surface has been investigated
detail using ab initio evolutionary structure search.
Our results show the (111)-$I_{R(z)}$ surface is lower in en-
ergy than the earlier reported structures [26], and con-
firm that the classical ECR governs the reconstructions,
results in the formation of novel bridging bonds between
the $B_i$ and $B_p$ atoms, leading to the metal-semiconductor
transition. In particular, significant charge transfer is re-
ponsible for the unique polar-covalent bonds between
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Bader charges for

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