Two-Dimensional Boron Icosahedral Structures

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Abstract

Two-dimensional (2D) materials beyond graphene (e.g., hexagonal boron-nitride sheet [1], transition metal dichalcogenides layered structures [2], and phosphorene [3]) are receiving much attention in the post-graphene era [4,5] because of their unique electronic and optical properties and their promise in nanoscale electronic and optoelectronic applications. Other 2D materials such as silicene and germanene [6], which are monolayers of silicon or germanium, respectively, have also been predicted and investigated extensively. Meanwhile, boron, a nearest-neighbor of carbon, has been considered to be possibly another element that can form 2D structures. However, in contrast to carbon, silicon, and germanium, boron is an electron-deficient element which has the tendency to form either a three-center two-electron bond or a strong directional covalent bond that give rise to various allotropic structures. In particular, 2D boron monolayer sheets (also called borophene) have been proposed recently [7-10]. Unlike B_{36} sheet which has a small energy gap (~0.12 eV [11]), all other predicted borophene are metallic and have not yet been synthesized successfully. We report here other possible allotropes of 2D boron structures that have not been predicted previously through a structural optimization technique based on a semi-empirical Hamiltonian [11, 12]. Using this method, we had recently predicted novel 2D boron structures (referred herein as icosahedral \( \alpha \), \( \delta_6 \), and \( \delta_4 \) sheets) [13], containing icosahedra B_{12} as their building units, and which exhibited interesting bonding and electronic properties in many aspects. First, the three-center two-electron bonding between icosahedra B_{12} of the \( \alpha \) bulk (i.e., rhombohedral boron as shown in the inset of Fig. 1 (d)) transforms into a two-center bonding in these new allotropes of boron sheets (see the insets of Fig. 1 (a)-(c)). Second, in contrast to the previously predicted buckled \( \alpha \) and triangular boron monolayer sheets [9], these new 2D allotropes form a planar network. As shown in Fig. 1, the calculated electronic density of states (DOS) reveal semiconducting nature for the icosahedral \( \delta_6 \) and \( \delta_4 \) sheets, and a nearly gapless (or metallic-like) feature for the icosahedral \( \alpha \) sheet, respectively. We find the icosahedral \( \delta_6 \) sheet to be energetically most stable among all boron-based quasi 2D structures proposed so far and is the most likely synthesizable by bulk truncation along \{001\} face of \( \alpha \) bulk. Finally, a relatively low energy barrier (0.17 eV/atom) for the transition from the icosahedral \( \delta_6 \) sheet to the icosahedral \( \alpha \) sheet was found, suggesting a possible pathway to “produce” the icosahedral \( \alpha \) sheet from the icosahedral \( \delta_6 \) sheet, whereas it appears unlikely to “produce” the icosahedral \( \delta_4 \) sheet directly from the icosahedral \( \delta_6 \) sheet because of the high energy barrier (0.38eV/atom) for the transition. A likely pathway could be the route from the icosahedral \( \delta_6 \) sheet first to the icosahedral \( \alpha \) sheet and then to the icosahedral \( \delta_4 \) sheet, as the energy barrier for the icosahedral \( \alpha \) phase to transform to the icosahedral \( \delta_4 \) phase is relatively low (0.27eV/atom). Quite recently, ultrathin single-crystalline boron nanosheets have been fabricated [14]. Such nanosheets demonstrate superior electronic-optical performances and potential applications in field-emitters, interconnects, integrated circuits, and optoelectronic devices [14]. The transmission electron microscopy and selected-area electron diffraction