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Structure and stability of bilayer borophene: The roles of hexagonal holes and interlayer bonding

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ABSTRACT

Two-dimensional (2D) boron monolayers with diversity of structures and extraordinary physical properties have been extensively investigated using first-principles calculations. A series of boron bilayer sheets with pillars and hexagonal holes have been constructed. Many of them have lower formation energy than α-sheet boron monolayer. The structural stability and chemical bonding character of these boron bilayers are analyzed by charge density, electron localization function and Bader charge, indicating that the optimal proportions of pillars and hexagonal holes can be obtained by balancing the surplus electrons. Meanwhile, the distribution and arrangement of hexagonal holes can cause ignorable effect on the stability of structures. These findings pave the way for the structural diversity of 2D boron materials.

Introduction

Due to its flat honeycomb structures, peculiar electronic band structure, and high specific surface areas, graphene have achieved huge success in electronic, magnetic, optical, thermoelectric, catalysis and energy storage systems [1–4]. The boom of graphene has stimulated the research of other elemental two dimensional (2D) materials [5,6]. Similar to carbon, boron also possesses a short covalent radius and flexibility to adopt sp^2 hybridization, which results in planar boron clusters [7,8], cage-like boron fullerene [9–11], and one-dimensional nanotubes [12,13]. Intuitively, boron atoms are expected to form 2D graphene-like monolayer sheet (namely, borophene). However, boron has one fewer electron than carbon. The electron deficiency in boron renders hexagonal honeycomb structures being stable by accepting elections while the flat triangular structure has surplus electrons in the antibonding states [14].

Thus, the biggest challenge in borophene synthesis is how to balance the surplus electrons. In this regard, hexagonal hole incorporation [15–19] and metal substrates passivation [20–22] are demonstrated as two effective methods. Taking the advantage of the balance of two-center and three-center bonds, Tang et al. [14] proposed stable α- and β- boron sheet with holes doping in hexagonal lattice for the first time. Soon after, more stable 2D boron sheets, such as α_1-sheet, β_1-sheet [15], $g_{1/8}$-sheet and $g_{2/15}$-sheet [23,24] with mixed hexagonal-triangular motifs have been predicted using a similar self-doping approach [25–27]. In those boron sheets, hexagonal holes are served as scavengers of extra electrons from the filled hexagons [28].

Depositing borophene on metal substrates is the alternative method to balance surplus electron of boron, which was firstly suggested for synthesis of the layered MgB_2 and TiB_2. Using first-principles calculations, Yakobson's group [20] considered the boron sheets on Cu, Ag, Au substrates and suggested that the deposition of boron atom on a Ag or Au(111) surface can result in growth of 2D boron sheets. Liu et al. [21] have demonstrated that the stability of monolayer boron sheets can be well stabilized by metal passivation of Cu (111) surface, and hexagonal holes can be easily formed via diffusion. Following these predictions, experimental fabrications of 2D boron sheets have also made a great achievement in recent years [29–32]. Mannix and co-workers [29] synthesized borophene with the character of anisotropic and out-of-plane buckling on Ag(111) surface. Feng et al. [31] fabricated β_{12} sheet and χ_3 sheet with different arrangements of periodic holes on Ag(111) substrate, which are inert to oxidization.

In line with the continuous advances in the prediction and fabrication of boron sheets, their novel properties and potential device applications become a rapidly growing area [33–38]. Zhang et al. [39] found that borophene have superior flexibility and elasticity that are even comparable to graphene. In addition, the mechanical properties could be tailored by regulating hexagonal holes density, showing promise perspective in flexible devices. Intrinsic phonon-mediated superconductivity was predicted in 2D boron sheet at the critical temperature about 20 K [40,41]. As an anode material, borophene enhances the capacity of Li ion batteries and outperform graphite anode [42–44].

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To fulfill those applications, some issues are dispensable to be solved. Since monolayer boron sheets must be synthesized on metal substrates, how about the bilayer boron sheets? Can bilayer boron sheets be peeled off from substrates and exist freely? If so, how about the specific distributions of stable atomic structures? How to balance the surplus electrons? What interaction and charge transfer between the two layers? What are the main differences between monolayer and bilayer boron sheets and which one is more stable? How does the arrangement of hexagonal holes and pillars affect the structural stability and electronic properties?

To answer these questions, herein we systematically investigate the structure, stability, chemical bonding character and electronic properties of a variety of boron bilayers. Our calculations show that the formation energy of plenty of boron bilayers composed with pillars and hexagonal holes is lower than that of the most stable $g_{1/8}$-sheet boron monolayer. The formation energies for these bilayers are reduced by self-doping between different coordinated boron atoms. The structural stability of these boron sheets are closely related to the distribution and ratio of hexagonal holes and interlayer pillars. Our theoretical results demonstrate a new electron balance approach for pure 2D boron sheets arising from interlayer interaction. This undoubtedly enlarges the family of 2D boron sheets and provides guidance in designing novel boron-based materials for experiments.

Computational methods

Density functional theory (DFT) calculations [45] were performed by the Vienna *ab initio* simulation package (VASP) [46], using the planewave basis set with energy cutoff of 500 eV, the projector augmented wave (PAW) potentials [47,48], and the generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof (PBE) [49] for the exchange-correlation interaction. The Grimme's D3 scheme of dispersion correction [50] was used to account for the long-range van der Waals interaction. A vacuum region of 18 Å was added to the vertical direction to eliminate the interactions between the neighboring layers. The Brillouin zones of the supercell were sampled by uniform **k** point meshes with spacing of 0.03/Å. The model structures were fully optimized for both cell and ionic degrees of freedom with thresholds for the total energy of 10^{-5} eV and the forces on each atom of 0.03 eV/Å, respectively.

To describe the stability of a 2D boron sheet, we define the formation energy E_{form} as:

$$E_{form} = (E_t - N \times E_B)/N \quad (1)$$

where E_t is the total energy of boron bilayer or monolayer, E_B is energy per atom in the boron solid of α phase, N is the number of boron atoms in boron monolayer or bilayer sheets.

Results and discussion

Bilayer boron sheets without hexagonal holes

Here we explore various possible configurations of bilayer boron sheets. There are two key parameters to characterize a bilayer sheet. First, two boron atoms from the upper and lower layers form a direct chemical bond, which is named as a pillar. Second, the electron deficiency of boron atoms in triangular lattice results in different arrangements of hexagonal holes. To better characterize the structural models, pillar density η_1 and hexagonal hole density η_2 [12,43] are defined as:

$$\eta_1 = \text{Number of atoms forming pillars}/\text{Number of atoms in the unit cell} \quad (2)$$

$$\eta_2 = \text{Number of hexagonal holes}/\text{Number of atoms in the original sheet} \quad (3)$$

For the sake of simplicity, we start from constructing a variety of boron bilayer sheets without hexagonal holes to examine the effect of pillar density on stability of structural models. The structural and energetic information of these models are summarized in Fig. 1. In all these structures, boron atoms can be classified into two

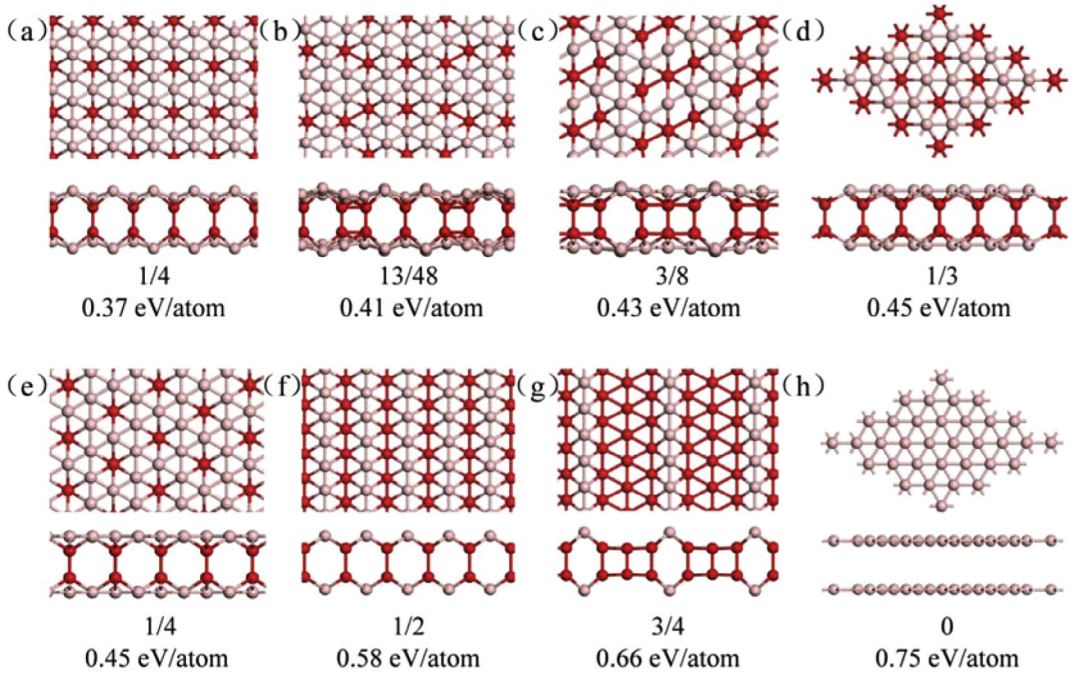

Fig. 1. Atomic structures of boron bilayers with different pillar density η_1 labeled by (a), (b), ... (h). The boron atoms at top and bottom planes and stack in top and bottom planes are labeled by pink and red color, respectively. The pillar density η_1 (upper) and formation energy E_{form} (lower) are given below each structural model. Among them, Boron bilayer structures in Fig. 1a, c, d, g and h are dynamically stable confirmed by their phonon density of states.