Physica E 91 (2017) 106–112

Contents lists available at ScienceDirect

Physica E

journal homepage: www.elsevier.com/locate/physe

Electronic and magnetic properties of pristine and hydrogenated borophene nanoribbons

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ARTICLE INFO

Keywords:
Borophene
Nanoribbon
Magnetic
Metal-semiconductor transition
Density functional theory

ABSTRACT

The groundbreaking works in graphene and graphene nanoribbons (GNRs) over the past decade, and the very recent discovery of borophene naturally draw attention to the yet-to-be-explored borophene nanoribbons (BNRs). We herein report a density functional theory (DFT) study of the electronic and magnetic properties of BNRs. The foci are the impact of orientation (denoted as BxNRs and ByNRs with their respective periodic orientations along x- and y-axis), ribbon width (N_x, N_y=4–15), and hydrogenation effects on the geometric, electronic and magnetic properties of BNRs. We found that the anisotropic quasi-planar geometric structure of BNR and the edge states largely govern its electronic and magnetic properties. In particular, pristine ByNRs adopt a magnetic ground state, either anti-ferromagnetic (AFM) or ferromagnetic (FM) depending on the ribbon width, while pristine BxNRs are non-magnetic (NM). Upon hydrogenation, all BNRs exhibit NM. Interestingly, both pristine and hydrogenated ByNRs undergo a metal-semiconductor-metal transition at N_y=7, while all BxNRs remain metallic.

1. Introduction

The discovery of graphene [1] ushers in an era of two-dimensional (2-*d*) atom or unit cell thick materials, from boron nitride [2–5], transition-metal dichalcogenides (TMDCs) [6–9], phosphorene [10–12], to silicene [13–16]. These materials exhibit novel electronic, magnetic, optical, and mechanical properties, thereby promising next-generation technology devices. In particular, the carbon-based atom-thick 2-*d* or one-dimensional materials, namely, graphene and graphene nanoribbons (GNRs), have become a new paradigm in condensed matter physics and device engineering research [17–29]. From graphene to GNRs, the change is not merely morphological. Compared to graphene, GNRs exhibit many novel electronic and spin transport properties [21,27–29], for example, GNRs with width less than 10 nm obtain an electronic band gap [21,27,28] owing to the contribution of edge states. While graphene is a zero-gap semimetal, both zigzag graphene nanoribbons (ZGNRs) and armchair graphene nanoribbon (AGNRs) are semiconductors [26]. In addition, hydrogenated ZGNRs adopt an anti-ferromagnetic (AFM) ground state along with a ferromagnetic (FM) meta-stable state, hydrogenated AGNRs are non-magnetic (NM), while graphene is NM [26]. With increasing ribbon width, GNRs crossovers to NM and the band gap diminishes.

Boron (B), carbon's nearest neighbor in the periodic table of chemical elements, is interesting in its own right [30,31]. The bonding between B atoms is more complex than in carbon as both 2-center and 3-center B-B bonding configuration are allowed, resulting in a wide variety of bulk B allotropes. For example, boron can form fullerene-like cage, B_{40}^{-} [32]. Various prototypes and synthesis mechanisms of boron-based 2-*d* nanostructures have been discussed theoretically [33–39]. Piazza et al. provided first experimental evidence of quasi-planar B_{36} cluster with a central hexagonal vacancy [33]. However, the synthesis of the B analogue of graphene, aka borophene, is unsuccessful until the recent work by Mannix et al. [40] They found that borophene adopts a corrugated (buckling) quasi-planar structure, in contrast to the planar honeycomb hexagonal lattice of graphene [1] due to the electron deficiency of boron compared with the carbon.

Furthermore, it is confirmed by scanning tunneling microscope (STM) measurements that borophene is a high anisotropic metal [40], in contrast to isotropic zero-gap semimetallic graphene. Peng et al. conducted first- principles calculations study of the electronic structure, bonding characteristics, optical and thermodynamic properties of borophene [41]. They found that borophene has high optical transparency and electrical conductivity, making it a promising candidate for transparent conductors used in photovoltaics. Xu et al. [42] combined

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http://dx.doi.org/10.1016/j.physe.2017.04.014
Received 23 February 2017; Received in revised form 5 April 2017; Accepted 18 April 2017
Available online 19 April 2017
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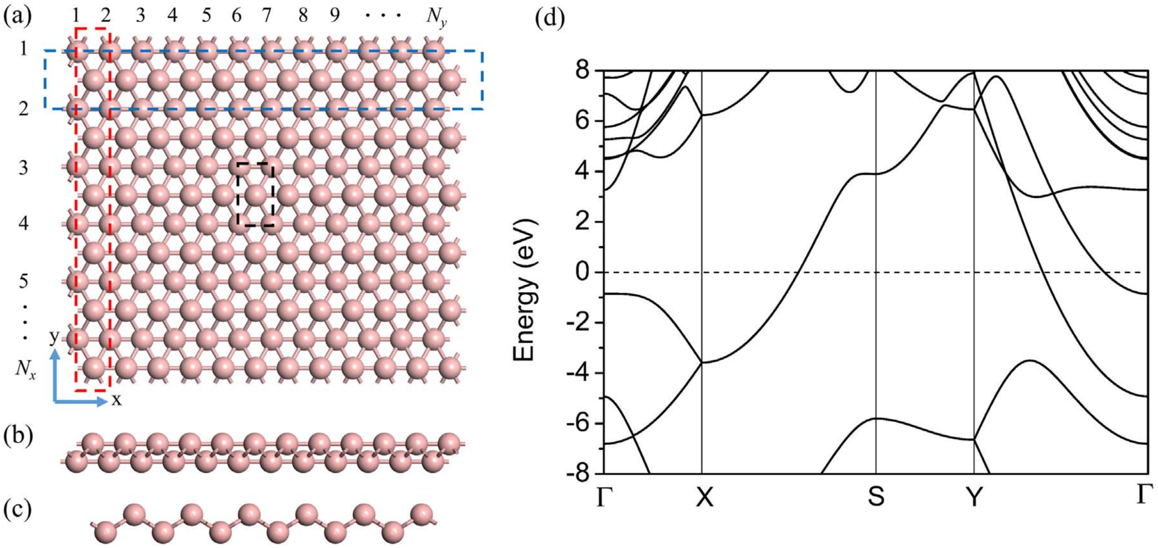

Fig. 1. (a) Top view, (b) side view along y-axis, (c) side view along x-axis of borophene, and (d) electronic band structure of borophene. The pink balls denote boron atoms. BxNR and ByNR are marked by the red and blue dashed rectangular, respectively. The unit cell of borophene used in the calculation is denoted by the black dashed rectangular. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

high-throughput screening with a first-principles method to demonstrate a novel growth mechanism of borophene from clusters and ribbons on Ag(111) plane. Penev et al. [43] theoretically predicted that borophene forming on a metal substrate should exhibit intrinsic phonon-mediated superconductivity, with estimated critical temperature in the range of $T_c \approx 10–20$ K. Zhang et al. [44] found that the storage capacity of borophene-based Li-ion and Na-ion batteries is several times higher than the commercial graphite electrode and the highest among all the 2D materials discovered to date.

In analogy with the research focus shift from graphene to GNRs mentioned above, it is compelling to study the electronic and magnetic properties of borophene nanoribbons (BNRs). BNRs might be realized either by cutting the synthesized borophene, or by patterning epitaxially grown borophenes. These methods have attained considerable success in making the graphene nanoribbons (GNRs) [23–25].. Since borophene is highly anisotropic. The orientation of BNR is expected to play an important role. In addition and in general, the impact of dangling bond of the edge atoms (i.e. the edge states) must be taken into account. To date, the works on BNRs are sparse.

We in this work conducted a systematical study on the geometric, electronic and magnetic properties of BNRs. The size effects, namely the ribbon width effects on the geometric, electronic and magnetic properties, are carefully examined. We compared the pristine and hydrogenated BNRs to help elucidate the impact of edge states. This paper is organized as follows. Firstly, we introduce and validate the calculation methods applied in this work. Optimized geometric (crystal) structures of pristine BNRs are obtained. Secondly, geometric, electronic and magnetic properties of pristine BNRs with different orientations and ribbon widths are discussed. We compare the case of BNRs with GNRs on several occasions. Finally, we study the impact of edge states on the geometric, magnetic and electronic properties of BNRs by implementing hydrogenation.

2. Computational methods

The equilibrium structures of BNRs are fully optimized by employing density functional theory (DFT) as implemented in QUANTUM ESPRESSO package [45]. The generalized gradient approximation (GGA) [46] of Perdue-Burke-Ernzerhof (PBE) was used as the exchange-correlation functional. The interaction between electrons and ions is modeled by using the ultrasoft pseudopotential. The cutoff for the kinetic energy was set to 50 Ry (1Ry=13.60569 eV) for the plane-wave expansion of the electronic wave functions. The charge-density cutoff was kept at 500 Ry. The Brillouin zone integration was performed using the Monkhorst-Pack scheme [47] with 13 meshes along periodic orientation. In order to eliminate image interaction, a large vacuum layer of 20 Å is used along non-periodic direction. Spin-polarized calculations were employed for geometric optimization and physical properties calculations. All the structures were fully optimized until the total energy converged to at least 10^{-6} Ry, and the forces between atoms became smaller than 10^{-4} Ry/Bohr.

In order to examine the validity of the plane-wave method discussed above. Parallel calculation was carried out using ADF/BAND package [48,49], which is also based on DFT. Different from the plane wave method in QUANTUM ESPRESSO, ADF/BAND adopts Slater-type local basis functions. In this calculation, slater-type local basis functions of triple-ζ quality with one polarization function (TZP) were used as basis set and a small frozen core approach was adapted. The parallel spin-polarized calculations were also carried out using the PBE [46] exchange correlation functiona. The Wiesenekker-Baerends scheme [50] was used to sample k-point mesh over the Brillouin zone. The Becke fuzzy cells integration scheme [51] was employed, where the integration parameter set to "good", resulting in 59 irreducible k-points for the 2-*d* borophene. For the BNRs, the integration parameter was also set to "good" except for the *k*-space sampling was kept fixed at 31 for consistency, resulting in total 16 k-points in the irreducible wedge. In order to take the scalar relativistic effects into account, Zero Order Regular Approximation (ZORA) [52] was included in all calculations.

3. Results and discussions

3.1. Geometric and electronic structure of borophene

The geometric structures of BNRs are displayed in Fig. 1(a)–(c). The optimized lattice parameters of borophene are **a**=1.616 Å and **b**=2.868 Å with space group *Pmmn* (orthorhombic), in comparison, the lattice parameters calculated using ADF/BAND are **a**=1.615 Å and **b**=2.871 Å. The calculated thickness is ~0.9 Å (cf. Fig. 2(b) and (c)). It is worth noting that (*i*) unlike graphene that is one-atom thick, borophene adopts a quasi-planar corrugated (buckling) structure; and (*ii*) unlike graphite and graphene, bulk boron cannot be attained by simple stacking borophene. The calculated electronic band structure indicates that borophene is a metallic along Γ-Y direction but has a band gap along Γ-X direction (Fig. 1(d)). Both the lattice parameters

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