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Line defects in boron nitride nanostructures: A first-principles study

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ABSTRACT

Using first-principles calculations we have explored the structural reconstruction of a special type of line defect (LD), formed as the result of a defective growth of a given monolayer (ML) or nanoribbon (NR). More specifically, we have studied the presence of tetragonal rings at boron nitride monolayers (BNMLs) and zigzag boron nitride nanoribbons (ZBNNRs). Different reconstruction processes are observed forming different types of LD depending on the nature of the atoms into the grain boundary between two BN domains as well as the structures type. The structural, magnetic, energetic, and electronic properties of the reconstructed BNMLs and ZBNNRs are calculated. These structures show a wide range of electronic structures going from semiconducting to semimetallic and metallic.

1. Introduction

Hexagonal boron nitride (h-BN) is a synthetic material, presenting a honeycomb configuration, equal number of boron (B) and nitrogen (N) atoms at its structure and sp^2 hybridization, very similar to the one shown by the graphene [1]. Comparing the h-BN to a graphene layer it is observed that a pair formed by one B and one N atoms are isoelectronic with the pairs of carbon (C) atoms. Also, the B, N and C atoms present quite similar values for the atomic radii. BN nanostructures, such as zero dimensional (0D) nanocones (BNNCs), unidimensional (1D) nanotubes (BNNTs) and nanoribbons (BNNRs), and bidimensional (2D) monolayers (BNMLs) have been the subject of extensive theoretical and experimental studies since these materials offer new possibilities for technological applications [1–6].

BNMLs show a rich variety of physical behaviour, such as a wide direct gap in the ultraviolet region [7], high mechanical stiffness [8], thermal conductivity [9], oxidation resistance [10], exhibits high transparency [11], and low coefficient of friction at high temperatures [12]. BNMLs are synthesized through different techniques such as micromechanical cleavage [13], chemical exfoliation [14], and chemical vapour deposition [3].

BNNRs can be generated by cutting BNMLs off. Depending on the way the cut is performed the BNNRs can present different forms and edge types known as armchair boron nitride nanoribbons (ABNNRs) and zigzag boron nitride nanoribbons (ZBNNRs). Exotic electronic and magnetic properties can arise when we cut BNMLs into BNNRs. For example, the electronic structure and magnetic ordering are strongly dependent on the ribbon width, edge structure and termination [5]. Also, it was shown that the energy gap can be significantly reduced by the application of a transverse electric field and even completely closed at a critical field magnitude, which value decreases with increasing ribbon width [15]. Finally, it was seen that BNNRs present half metallicity along their edges [16]. These remarkably electronic and magnetic properties would make the BNNRs good candidates to be used as active parts of nanoelectronics and spintronics devices. At these days, BNNTs unzipping is a popular approach for BNNRs production [18,17].

However, the utilization of these materials as functional parts of real technological devices depends on the ability to adjust the wanted properties at nanoscale. There are several possible ways to alter the BN nanostructures properties and here we will focus on the incorporation of defects. It is known that structural and substitutional defects are inevitably created during any growth process, and thus, learning to use them in our favour can be advantageous. For example, these type of defects can be used to tune the electronic and magnetic properties of nanomaterials, offering new application possibilities [19]. An interesting type of defect is the one called line defect (LD). Recently, Chen et al. synthesized a LD composed by two pairs of pentagonal rings surrounding one octagonal ring (558-LD) replacing the hexagons in a graphene sheet [20]. In another work, Li et al. proposed a way to generate

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one stable LD, formed by tetragonal carbon rings (4-LD), at a graphene sheet [21]. A similar type of LD was observed at a MoS_2 sheet [22]. Auwärter et al. have demonstrated, experimentally, that h-BN growth on Ni results in triangular islands with two different domains with a LD between them [23]. The experimental study of LDs in graphene and BN nanostructures has motivated the study of BNMLs and BNNRs with LDs [24–26].

At this context, using first-principles calculations, we perform a comprehensive study of how different reconstruction processes are formed with the inclusion of a 4-LD in BNMLs and ZBNNRs. We report three new types of LDs at the grain boundary. The properties of the reconstructed BNMLs and ZBNNRs are calculated. These structures show a wide range of electronic structures going from semiconducting to semimetallic and metallic.

2. Methodology

We have performed first-principles calculations based on the density functional theory (DFT) [27], as implemented at Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code [28,29], to investigate how different reconstruction processes are formed due to the inclusion of different 4-LD in BNMLs and ZBNNRs. We make use of norm-conserving Troullier–Martins pseudopotentials [30] in the Kleinman–Bylander factorized form [31] and a double-ζ basis-set composed by numeric atomic orbitals with a cuttoff radius of $\approx 15.0\,\AA$. The generalized gradient approximation (GGA) [32] with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used [33]. The geometric optimization was performed by minimizing the systems total energy until the residual forces are less than 0.1 eV/Å.

In Fig. 1(a) we present a schematic structural model for the BNML, where we have two domains with different (mirrored) orientations and, between these domains, we can introduce B, N and C atoms creating BNMLs (up) and (or) ZBNNRs (down) with different atoms at a 4-LD at grain boundary. In Fig. 1(b) we have the BNML and ZBNNR pristine structures; in Fig. 1(c) we can observe a tetragonal ring line defect (4-LD) formed by the inclusion of a N atoms line in the middle of the sheet ($BNML_N$ and $ZBNNR_N$). In Fig. 1(d) and (e) we show a 4-LD formed by the insertion of B and C atoms ($BNML_B$ and $ZBNNR_B$) and ($BNML_C$ and $ZBNNR_C$), respectively. In Fig. 1(f) and (g) we show a 4-LD formed by the inclusion of pairs of CN ($BNML_{CN}$ and $ZBNNR_{CN}$) and CB atoms ($BNML_{CB}$ and $ZBNNR_{CB}$), respectively. Finally, in Fig. 1(h) we show a 4-LD formed by the inclusion of NB pairs ($BNML_{NB}$ and $ZBNNR_{NB}$).

3. Stability

The calculation of the energetic stability of various BNMLs and ZBNNRs is performed using a zero-temperature approach based on the prior determination of convenient chemical potentials, as described in [34–36]. In this approach, the formation energy by atom (E_{for}) can be written as:

$$E_{for} = (E_{tot} - n_C\mu_C - n_B\mu_B - n_N\mu_N - n_{HN}\mu_{HN} - n_{HB}\mu_{HB})/n_t, \quad (1)$$

where E_{tot} is the total energy calculated by SIESTA, n_C, n_B, n_N, n_{HB}, and n_{HN} are the number of C, B, N atoms and H–B and H–N bonds,

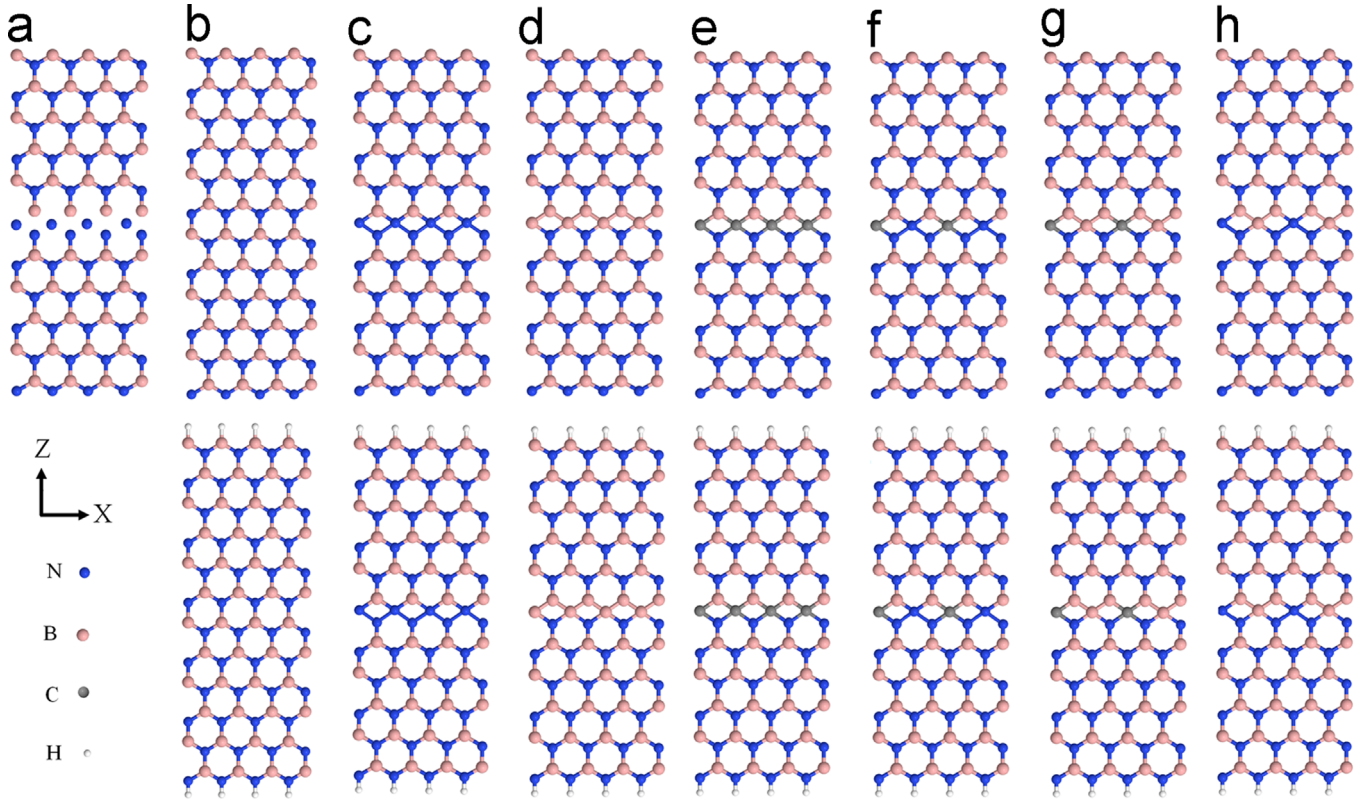

Fig. 1. (Colour online) Pictorial scheme for the studied boron nitride monolayers (BNMLs) (up) and zigzag boron nitride nanoribbons (ZBNNRs) (down) before optimization. (a) Structure model of a LD in h-BN with two domains presenting different orientations. (b) BNML and ZBNNR pristine, and presenting a 4-LD composed by: (c) Nitrogen ($BNML_N$ and $ZBNNR_N$), (d) boron ($BNML_B$ and $ZBNNR_B$), (e) carbon ($BNML_C$ and $ZBNNR_C$), (f) carbon–nitrogen ($BNML_{CN}$ and $ZBNNR_{CN}$), (g) carbon–boron ($BNML_{CB}$ and $ZBNNR_{CB}$) and (h) nitrogen–boron ($BNML_{NB}$ and $ZBNNR_{NB}$) atoms. Hydrogen, boron, carbon and nitrogen atoms are represented by the white, light pink, gray, and dark blue spheres, respectively.