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Stability and electronic structure of BN negative disclination

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Abstract

We investigate, using first-principles calculations, the stability and electronic structure of disclinations, in nitride boron monolayers, with angle of $\theta = -60^\circ$, called saddle-like compounds. Such structures present antiphase boundaries (APBs) that cause a reduction of the work function of the nanosaddle, relative to the BN bulk value, by as much as 3.5 eV. Our results also indicate that nanosaddles with a lower number of B–B and N–N are the most stable among the studied structures. In addition, we find that APBs with carbon can enhance their stability.

Keywords: Nanostructure; Nanosaddle; Stability; Nitride boron

1. Introduction

Curved nanoscale structures, of which the best known are fullerenes and nanotubes, have been the focus of increased scientific and technological interest, due to their unique electronical and mechanical properties [1–3]. Boron nitride (BN) and carbon can be found in similar structures, from diamond and graphite form bulks to nanostructures such as nanotubes [4], conical sheets [5–7], and saddle [8,9]. However, unlike carbon, BN compounds can contain three types of covalent bonds, namely B–N, N–N, and B–B bonds. This leads to a qualitative difference between BN and carbon in the formation of the graphite-derived curves surfaces that are found in nanostructures.

In 1991, Mackay and Terrones [10] proposed that the inclusion of carbon rings with more than six atoms in a graphite or nitride boron hexagonal sheet could produce stable periodic arrangements with negative curvature. These new hypothetical arrangements are called Schwarzites [8]. On the other hand, the incorporation of heptagon, pentagons, and other defects into a hexagonal network of carbon or nitride boron nanotubes increases the local curvature and it can lead to the closure of the tubes [11]. In nanotubes, the introduction of heptagons leads to changes in nanotube size and its orientation. Theoretical calculation has been carried out to investigate the electronic structure and stability of the carbon structure with positive and negative disclinations [12–15]. In carbon, energy minimization leads to compounds made of 60° disclinations (conical sheet) with isolated pentagons at the apex. Carbon fullerenes are built from such structures. In BN, fullerene-like structures are formed from 120° disclinations. These 120° disclinations are usually modeled as having a four-membered ring at the apex, but theoretical calculation indicate that non-stoichiometric BN fullerenes, consisting of pentagon pairs replacing the four-membered rings, may be energetically favored, depending on the stoichiometric condition of growth [16,17]. Recently [18] showed that cones with a line defect, that contain B–B or N–N bonds, can be more stable than those without one.

In the present work, we investigate the relative stability of BN nanosaddle, a heptagon, with N–N and B–B bonds, for N-rich and B-rich environments. Our first-principles results indicate that BN structures with a negative curvature, disclination of -60°, are more stable than those with a positive curvature, angle of 60°. We also find that formation energy depends on the number

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of B–B and N–N bonds. The more stable nanosaddles are those that present the minimum number of wrong bonds, under both environments. We also showed that structures involving full carbon incorporation are among the most stable. We also studied the electronic structure of a finite-size saddle with an angle of −60° of disclination. Our main conclusion is that BN structures containing carbon, in the antiphase boundaries (APBs), reduce the work function, relative to the bulk BN value, by as much as 3.5 eV.

Our calculation is based on the density functional theory [19] as implemented in the SIESTA program [20]. We make use of non-conserving Troullier–Martins pseudopotentials [21] in the Kleinmann–Bylander factorized form [22] and a double-ζ basis set composed of a numerical atomic of finite range. Polarization orbitals are included for nitrogen, boron, and carbon atoms, and we use the generalized gradient approximation [23] (GGA) for the exchange-correlation potential. All the geometries are fully relaxed, with residual forces smaller than $0.1\,\mathrm{eV/\mathring{A}}$. If the maximum difference between the output and the input on each element of the density matrix in an SCF cicle is 10^{-4}, then the self-consistency has been achieved.

Before discussing the results it should be noted that the SIESTA method does not include the treatment of spin–orbit interaction; hence, it is not possible to discuss such a subject on this basis of calculation.

Fig. 1 shows six of the most stable structures found in our study. Note that each contains a −60° disclination,

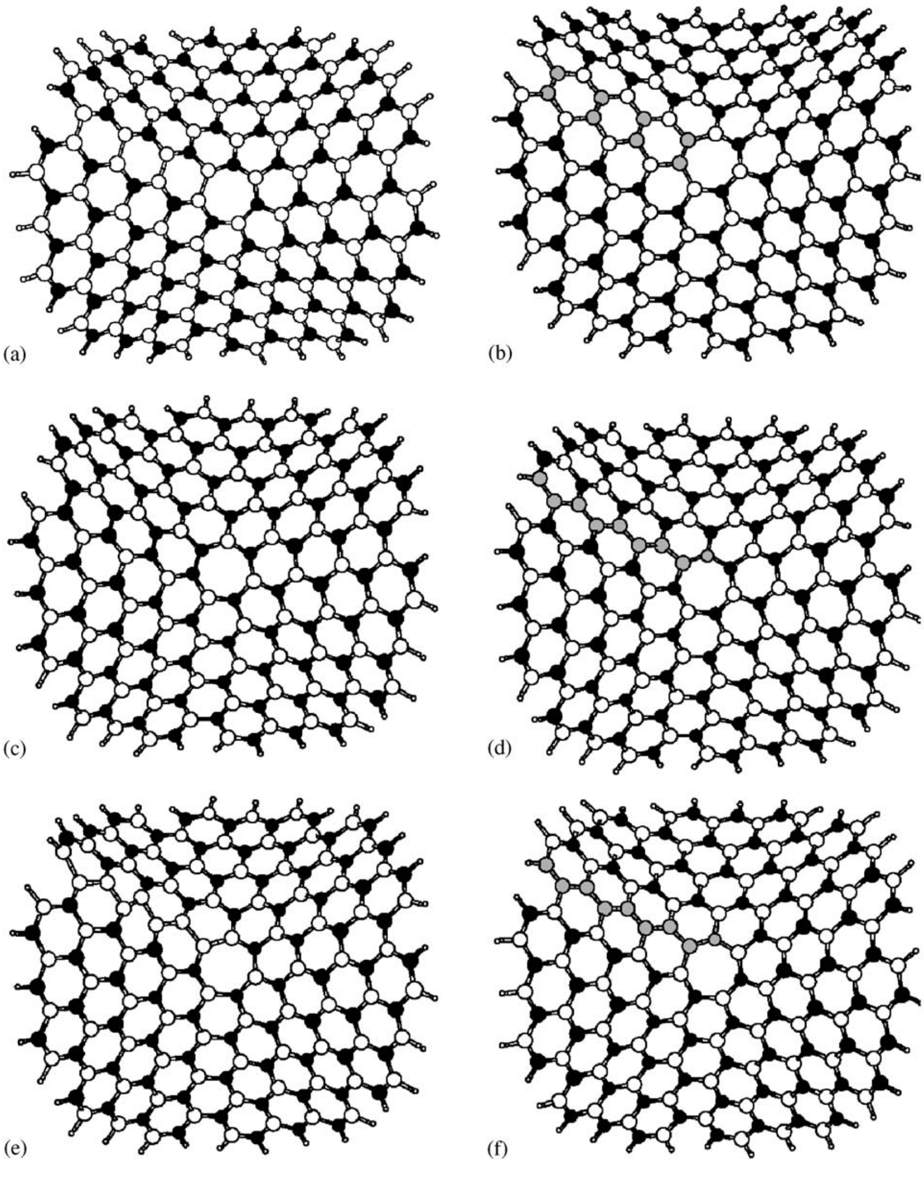

Fig. 1. Six saddle-like structures with disclination of −60°: Carbon, nitrogen, and boron atoms are represented by gray, black, and white, respectively. Hydrogen atoms saturate the dangling bonds at the edges. (a), (b), and (c) show a parallel APB of boron, carbon, and nitrogen, respectively. (d), (e), and (f) show zig-zag APB of carbon–nitrogen, boron, and carbon–boron, respectively.

leading to the formation of an APB. We consider two kinds of APBs: one contains a sequence of parallel (B–B, C–C, N–N) bonds, as shown in Figs. 1(a)–(c), and the other a sequence of zig-zag (C–C, B–B, C–C) bonds. These are denoted as molecular APB and zig-zag APB, respectively. Such structures are composed for 196 atoms, where 161 BN and 35 hydrogen atoms exist. The B–N bond length values are 1.47 and 1.45 Å for bonds in and outside of the pentagon, respectively. This is consistent with results described in earlier works [24].

2. Relative stability

In order to address the energetics of nanosaddle in boron-rich and nitrogen-rich environments, we introduce the theoretically determined chemical potential for nitrogen μ_N and boron μ_B. The environment is determined by the specific atomic reservoir employed. In the N-rich environment, μ_N is obtained from solid nitrogen in the α-phase, while a metallic $\alpha - \beta$ phase is used as the reservoir for the β-rich environment, as described in [25,26]. In both cases, μ_N and μ_B are linked by the thermodynamic equilibrium condition,

$$\mu_N + \mu_B = \mu_{BN}^{layer}, \tag{1}$$

where μ_{BN}^{layer} is the chemical potential per BN pair in the infinite, planar BN sheet. Since we are dealing with infinite clusters, we use hydrogen atoms to saturate the dangling bonds at the edges. To take these H–B and H–N bonds into account, we introduce the respective chemical potentials, μ_{HB} and μ_{HN}, that allow us to write the formation energy of the saddle-like structure as

$$E_{form} = E_{tot} - n_B\mu_B - n_N\mu_N - n_{HN}\mu_{HN} - n_{HB}\mu_{HB}, \tag{2}$$

where E_{tot} is the calculated total energy of the cluster, n_B and n_N are the numbers of B and N atoms, and n_{HN} and n_{HB} are respectively the number of H–B and H–N bonds, that appear due to saturation of the dangling bonds at the edges by hydrogen atoms as shown in Fig. 1. A first constraint on the hydrogen chemical potential is imposed by using a finite planar sheet of BN as reference, and ascribing a null value to its formation energy. This leads us to write its total energy as

$$E_T^{sheet} = n_{BN}\mu_{BN}^{layer} + n_H\mu_H, \tag{3}$$

where $\mu_H = \frac{1}{2}(\mu_{BH} + \mu_{NH})$, and n_{BN} and n_H are numbers of B–N bonds and H atoms in the BN layer. Using the total energy calculation for an infinite monolayer and a finite sheet, we find that $\mu_H = -15.46$ eV.

From the definition of μ_H, we obtain $\mu_{HB}(\mu_{HN})$ once $\mu_{HN}(\mu_{HB})$ is known. The values of these parameters can be determined by choosing a convenient reservoir. In our calculations we use the ammonia molecule (NH_3) as a reservoir, obtaining $\mu_{HN} = -16.14$ eV and $\mu_{HB} = -14.78$ eV in the N-rich environment, and $\mu_{HN} = -15.23$ eV and $\mu_{HN} = -15.69$ eV in the B-rich environment.

Table 1
Formation energies (in eV/atom) of the boron nitride saddle-like and cone-like structures

APB	Nanosaddle		Nanocone	
	$E_{form}/n(B)$ N-rich	$E_{form}/n(N)$ B-rich	$E_{form}/n(B)$ N-rich	$E_{form}/n(N)$ B-rich
Mol-B	0.17	0.08	0.24	0.12
Mol-CB	0.29	0.11	0.42	0.18
Mol-CN	0.08	0.26	0.12	0.37
Mol-N	0.08	0.17	0.12	0.24
Zig-B	0.31	0.14	0.43	0.20
Zig-CB	0.20	0.08	0.29	0.13
Zig-CN	0.06	0.18	0.10	0.26
Zig-N	0.15	0.32	0.22	0.44

The first column indicates the APB of each structure. The second and third columns indicate the formation energy for saddle-like models, positive disclination with angles of −60°. The fourth and fifth columns show the formation energy for cone-like models, negative disclination with an angle of 60°. Underlined values indicate the most stable structure.

The results obtained for the formation energies of the BN nanostructures, using the above procedure, are shown in Table 1 for −60° and 60° disclinations in both nitrogen-rich and boron-rich environments. As shown in Refs. [25,18], in a condition of chemical equilibrium, the relative stability of the structures is determined by the quantity E_{form}/n_{poor}, where n_{poor} is the number of atoms of the species for which the environment is poor [$n_B(n_N)$ in the N-rich(B-rich) case]. The underlined numbers in Table 1 indicate the most stable structures. A general trend that can be inferred from the numbers in the table is that structures with a negative disclination, −60°, are more stable than structures with a positive disclination, 60°. This stability can be explained by the fact that in the heptagonal rings there is very little mechanical strain, compared to positive disclination, thus preserving the sp^2-like nature. Indeed, as we can see in relaxed structures, the compounds present 121° and 106° angles for nanosaddles and nanocones, respectively. That is, the elastic energy required to fold a finite sheet into a cone is larger than the energy required for the formation of a saddle-like monolayer. Besides, we can verify that structures displaying the minimum number of B–B and N–N bonds, in their respective environments, are the most stable. In addition, we find that carbon incorporation leads to stable structures. This result permits us to conclude that such systems tend to maximize the B–N and C–C bonds, a result that agrees with that obtained with BCN monolayers [27–29].

3. Electronic structure

The electronic structures of the most stable BN nanosaddle with an angle of disclination of −60° are shown in Fig. 2. The general trend is that the presence of N–N bonds introduce occupied states in the lower half of the band gap, Fig. 2(b), while those associated with B–B bonds are unoccupied and in the upper half of the band gap, Fig. 2(a). An important feature shown in Fig. 2(c) is the increase in the energy of the highest occupied electron state for the BN positive disclination that contains carbon, when compared to the BN sheet.

It is known from semi-empirical calculation that the work function of the hexagonal BN, using the extended Huckel method, is given by 10.6 eV [30]. Using this value as reference, the new values of the structures described in Fig. 2 are given by 10.6, 9.4, 7.9, 6.6, and 3.7 eV for mol-B, mol-CB, mol-N, mol-CN, and zig-CN nanosaddles, respectively, Fig. 2. This result permits us to conclude that there is a decrease in the work function of all BN compounds that contain APBs, with the exception of the mol-B boundary, and a significant increase, Fig. 2c, in the energy of the highest occupied electron (for the case of zig-CN nanosaddle we have a significant increase by as much as 3.5 eV). This indicates that the BN nanosaddles in field emission devices would be very sensitive to the topology of the structures: those with APBs would be much better electron emitters than those without these line defects.

From Fig. 2, we can see that energy gap are obtained by 3.32, 0.16, 3.03, 1.52, and 1.1 eV, for mol-B, mol-CB, mol-N, mol-CN, and zig-CN compounds, respectively. A recent calculation, a self-consistent method for calculating the electronic structure crystal where the infinite one, is approximated by a progressively enlarging cyclic cluster placed in the madelung field by the remainder of the crystal, [31], obtained by an energy gap of 4.3 eV, using DTF and $L = 36$ (the parameter L is the number of points k). Therefore, we conclude that the gap width in all saddle-like compounds decreased when compared with the BN crystal. An important feature is that for mol-B and zig-CN structures, the width gap decreases by 4.14 and 3.2 eV, respectively, due to the presence of APB. This suggests that the APB in the BN nanosaddle could strongly affect the properties of BN layered materials.

We also investigate the case of polarization spin for BN monolayers with −60° disclination. We have found spin splitting for a structure with heptagons, since such structures display an odd number of electrons. Therefore we can conclude that structures, with an odd electrons number, display net spin. Therefore, angles of disclination −60°, −180°, and −300° present spin polarization.

4. Conclusions

In summary, we used first-principles calculations to address the question of the stability and electronic structure of boron nitride monolayers with negative disclinations. It was shown that negative disclination,

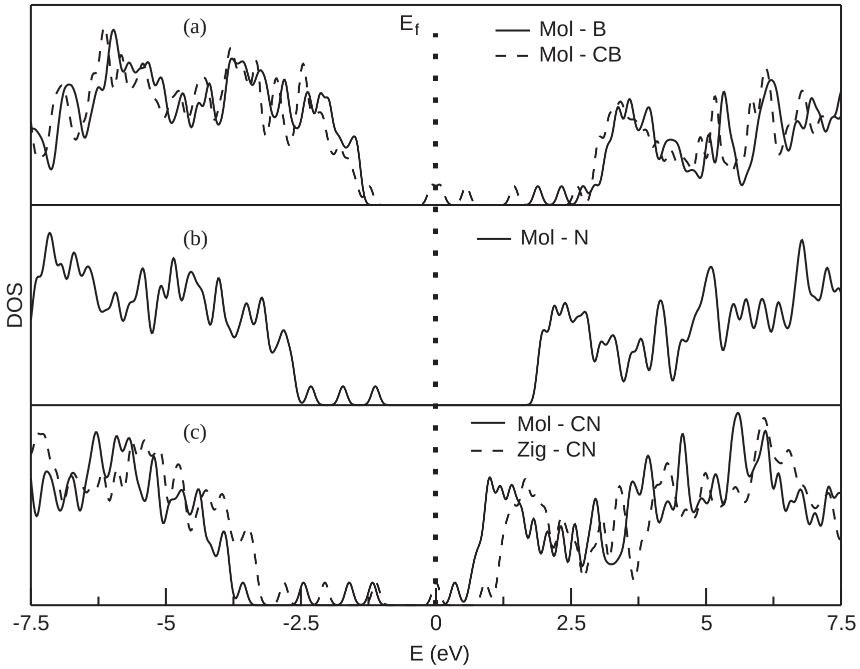

Fig. 2. Density of state of the most stable structures described in Fig. 1. The DOS (a) corresponds to Figs. 1(a) and (b); the DOS (b) corresponds to Fig. 1(c); finally, the DOS (c) corresponds to Figs. 1(d) and (f).

saddle, are more stable than positive disclinations, cone. In addition, we observed that the carbon incorporation in the nanosaddle leads to highly stable structures, leading us to conclude that the changes in the electronic structure of the nanosaddle containing carbon should strongly reduce the work function of these BN nanostructures. Besides, we find that negative disclination, with a heptagonal ring, with antiphase boundaries formed by B–B or N–N bonds introduce electron states in the energy-gap region. This behavior is analogous to that described in Ref. [18] for structures with positive disclination. Therefore, we can conclude that such states are due to wrong bonds, and they are not associated with curvature. We also find that states associated with B–B and N–N bonds appear close to the conduction and valence band edges, respectively. Our results suggest that changes in the electronic structure of the nanosaddle containing carbon should strongly reduce the work function of the BN structures, with important implications for understanding the field emission properties of these systems. We also investigated the case of placing boron or nitrogen, as substitutional impurity, on structures with a negative disclination, in the heptagon or outside the heptagon. In addition, it is shown that the structure displaying an odd number of electrons, for example disclinations with angles of -60°, has spin polarization.

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