Electronic and structural properties of two mirrored boron-nitride nanocones with 240^{o} disclination

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We studied, through first-principles calculations based on the density functional theory, the charge distribution, the density of states and the tip rearrangement of two mirrored boron nitride nanocones with 240$\mathring{A}$ disclination angles and separated from each other from 2$\mathring{A}$, 3$\mathring{A}$ and 10$\mathring{A}$ under the influence of an external electric field ranging from 0.5 V/$\mathring{A}$ to 1.1 V/$\mathring{A}$ applied along the axis. Changes at the charge distribution, density of states and tip configuration were observed with the variation of the cones separation distance and the magnitude of the external electric field.

Keywords: electronic structure, nanomaterials, nanocones, boron and nitrogen

I. INTRODUCTION AND METHODOLOGY

Boron nitride (BN) nanocones with a model of orderly stacked 240^{o} disclination, which is the smallest cone geometry ensuring the presence of B-N bonds only, were observed in 2000[1]. Those cones are known to present an apex formed by one hexagonal BN ring ending in two two-coordinated atoms. We suggested a new tip configuration for the boron nitride nanocones with 240^{o} disclination where the apex is composed by four pentagons sharing two three-coordinated atoms[2]. Due to their low dimensional tip structure and electronic properties, nanocones containing boron and nitrogen atoms were thought as possible field-emission materials[3]. In previous works we have shown that the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases with the increasing of the external electric field applied to those cones[4]. We also showed that charge tends to concentrate at the boron atoms at the tip of the cones and the HOMO and LUMO are localized at the same area when the external electric field is applied. In other words, our results reinforce the idea of using those new structures as parts of field-emission devices.

In the present work we calculate the electronic and structural properties of two boron nitride nanocones facing each other separated by 2Å, 3Å and 10Å under the effect of an external electric field ranging from zero to 1.1 V/Å. Each cone is composed by 62 boron and nitrogen plus 12 hydrogen atoms to saturate the dangling bonds at the base of the cone. The cones where labeled as R (for right) and L (for left) and were arranged in two different ways that we will call homogeneous (HO) and heterogeneous (HE). At the HE configuration cone R can be seen as if it was cone L rotated by 180° around the tip and 180° around the axis (in this way the B atom at L is in front of an N atom at R, see figure 1a). For the HO configuration we have cone R as if it was cone L rotated by 180° around the tip (in this way the B atom at L is in front of a B atom at R, see figure 1b). To make the analysis easier the cones were also divided in layers of atoms perpendicular to the cone axis and classified, as follow, from top to bottom of the cones: layer 1 is composed by the two atoms at the tip of the cone (one B and one N); layer 2 is composed by 10 atoms (five B and five N); layer 3 is composed by 14 atoms (seven B and seven N), Layer 4 and 5 are composed by 18 atoms each (nine B and nine N), H layers are composed by 12 H atoms at the end of the cone.

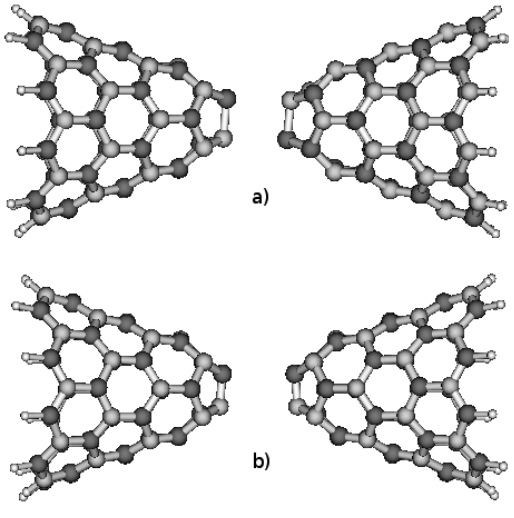

FIG. 1: Pictorial scheme of boron nanocones at the (a) heterogeneous (HE) and (b) homogeneous (HO) configuration.

All the calculations are done through first-principles calculations based on the density functional theory, as implemented in the SIESTA code[5]. Local density approximation (LDA) is used to treat the exchange and correlation functional[6, 7]. To expand the Kohn-Sham valence orbitals a linear combination of pseudo-atomic double zeta quality basis set with polarization functions is employed[8, 9]. The interaction between the ionic cores and the valence electrons is represented by norm-conserving pseudopotentials[10]. The supercell is a cubic box large enough to exclude the interaction between cones in adjacent cells and to avoid the presence of charges near the cell boundaries. The atomic positions of all atoms are fully optimized until forces are lesser than 0.05

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eV $\AA^{-1}$.

II. RESULTS AND DISCUSSIONS

One of the major problems when submitting physical systems to electric fields is to determine if such structures will remain stable. In this sense we have analyzed how the atoms at the tip behave geometrically with the variation of the distance and the magnitude of the external electric field. It was observed for the HE system with starting separation of 2Å, after the application of the electric field equal to 0.5 V/Å, that there is a small distortion of the tip atoms and the cone to cone distance is reduced to 1.5Å. This distance, however, is increased to 2.75Å when the magnitude of the field is equal to 1.1 V/Å. When the starting distance is equal to 3Å and the applied field equal to 0.5 V/Å the distance is reduced becoming 2.8Å and 2.4Å for the upper B-N and bottom N-B bonds (see figure 1), respectively. As soon as the electric field is enhanced to 1.1 V/Å we have a significant increase of the distance between the cones that becomes around 5.2Å. For the HO case with 2Å for starting cone to cone distance we observe that the boron-boron distance remains the same, for the electric field equal to 0.5 V/Å and the nitrogen-nitrogen distance increases becoming around 2.8Å. With the increasing of the external electric field magnitude to 1.1 V/Å those distances are decreased becoming 1.8Å for the B-B distance and 2.4Å for the N-N ones. Finally, for the case where the cones are separated by 3Å, the distance remains practically the same when the field is equal to 0.5 V/Å and is increased to 4Å when the electric field is equal to 1.1 V/Å. It is observed that the cone to cone distance varies according to the magnitude of the external electric field with a slightly distortion of the atoms at the tips of the cones, effect that emphasizes the little tip degradation of those structures. It was also observed that some hydrogen atoms at the end of the cones are totally unbounded after the application of the electric field.

For the densities of states of the systems we have the following results that can be seen at figure 2. We start by making a comparison between the two different separations (2Å and 3Å) of cone He. We can see, from figure 2, that the density of states (DOS) is pretty much the same for both separations, fact that is not true when we compare the 2Å case with the 10Å one where we can observe a small shift of the levels towards higher values of energy. Besides, there is a small peak just above Fermi energy for the system with separation equal to 10Å while no peak is observed for the one presenting 2Å separation. The same behavior is observed when we compare the system He with the Ho for the same cone-cone separation of 2Å, we see an energy shift for the levels below and above Fermy energy with a small peak arising for the Ho system only. Finally, when we compare the non field situation with the one where the external electric field magnitude is 1.1 V/Å we see a gap closure as shown in the figure 2. These results shown that there are several possibilities if we think about tailoring the electronic properties of BN nanocones that can behave like semiconductor structures or metallic ones. Besides the presence of isolated peaks close to Fermy energy can contribute with the custom made design of different types of electronic devices.

Next we are going to analyze the Mulliken charge distribution with and without the presence of the external electric field applied at the He and Ho systems when separated by 2 and 3Å. The Mulliken charge values at each layer is given by the simple average value (sum of the charge of all atoms of same species divided by the number of atoms of that species) except for layer 1 where we have only one atom of each species. From Table I, showing the results for the He system with the cones separation equal to 2Å, we can see that there is a charge concentration at B atoms at all layers together with a reduction of charge concentration at the N atoms. The same occurs for the H atoms at the end of the cones. For the Ho system the results are very similar with small charge concentration fluctuations.

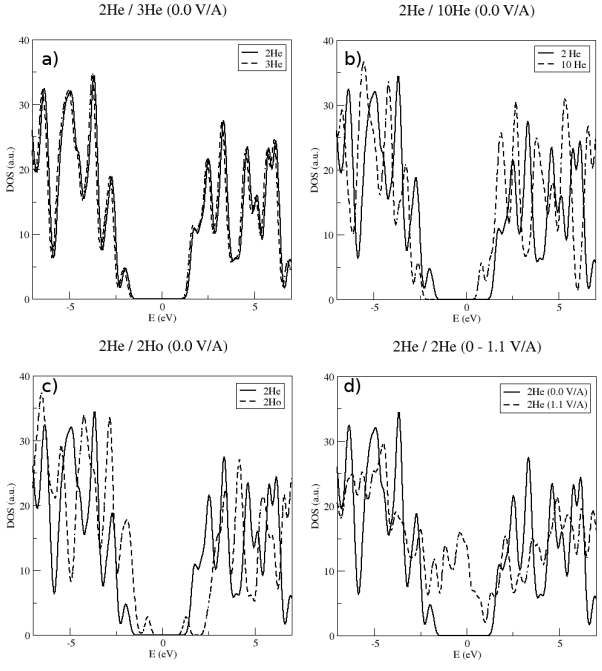

FIG. 2: Densities of states of the systems (a) He with separation equal to 2Å (solid line) and 3Å (dashed line) and no electric field applied, (b) He with separation equal to 2Å (solid line) and 10Å (dashed line) and no electric field applied, (c) He (solid line) and Ho (dashed line) with 2Å separation and no electric field applied, and (d) He with separation equal to 2Å and electric field ranging from zero (solid line) to 1.1 V/Å (dashed line).

TABLE I: Average Mulliken charge values per atom per layer for the system He with 2Å separation for the cones (R) and (L) at the non field situation and the electric field magnitude equal to 1.1 V/Å.

		He - 2Å			
Layers		L (0 V/Å)	R (0V/Å)	L (1.1 V/Å)	R (1.1 V/Å)
1	B	3.05	3.06	3.33	3.34
	N	4.99	4.99	4.56	4.64
2	B	3.13	3.13	3.57	3.54
	N	4.87	4.87	4.47	4.46
3	B	3.14	3.14	3.62	3.62
	N	4.86	4.86	4.38	4.38
4	B	3.16	3.16	3.61	3.64
	N	4.86	4.86	4.36	4.37
5	B	3.08	3.08	3.30	3.53
	N	4.88	4.88	4.29	4.36
H		1.00	1.00	1.05	1.05

After that we can analyze the behavior of the system where the cones are 3Å apart. For the layers 1 to 5 the behavior is pretty much the same as the one observed for the cones separated by 2Å. However, for the H atoms there is a reduction of charge concentration for the ones at the left side together with the increasing of the charge at the ones at the right side as can be seen in Table II. When we look at the charge behavior, the main difference between this work and our previous ones[2] is that the charge concentration occurs for all B atoms of the cone with the correspondent decreasing of charge concentration at the N atoms and not only at the ones located at the tip, as the external electric field is applied.

In summary, we studied the structural and electronic of boron-nitride nanocones with 240$\mathring{A}$ disclination presenting an apex composed by four pentagons. We have shown that there is little tip degradation with slightly geometric dislocation of the atoms at the tip with the application of an external electric field. By analyzing the densities of states of these systems we saw that there are good possibilities to tailor BN nanocones in order to have specific applications through energy gap variation. We have also seen that charge tends to migrate from the N atoms to the B ones as a trend, a different result when we compare with the situation when we have one isolated cone.

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TABLE II: Average Mulliken charge values per atom per layer for the system He with 3Å separation for the cones (R) and (L) at the non field situation and the electric field magnitude equal to 1.1 V/Å.

		He - 3Å			
Layers		L (0 V/Å)	R (0V/Å)	L (1.1 V/Å)	R (1.1 V/Å)
1	B	3.05	3.06	3.46	3.37
	N	4.98	4.99	4.64	4.62
2	B	3.13	3.13	3.54	3.52
	N	4.87	4.86	4.46	4.45
3	B	3.14	3.14	3.61	3.62
	N	4.86	4.86	4.64	4.38
4	B	3.16	3.16	3.59	3.63
	N	4.86	4.86	4.36	4.40
5	B	3.08	3.08	3.26	3.58
	N	4.88	4.88	4.27	4.45
H		1.00	1.00	0.97	1.40

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