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Theoretical study of Si impurities in BN nanotubes

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Abstract. Density functional theory is employed to investigate the electronic and structural properties of substitutional Si impurities in a (10,0) BN nanotube. For the Si_B case, the band structure shows a level centered on the Si atom crossing the Fermi energy and no net spin is found. The Si_N introduces three localized exchange splitted Si levels in the gap. The formation energies show that the Si_B is likely to be present at N-rich conditions.

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1 Introduction

Nanoscale materials are now the focus of many research activities looking for novel, specific and even unexpected properties. A great impulse to the studies of nanoscale materials was the discovery of carbon nanotubes by Iijima [1]. These carbon nanotubes were theoretically predicted and experimentally verified to present electronic properties that are dependent of their chiralities and diameters. Today, nanotubes of other materials like BN [2], $NiCl_2$ [3], MoS_2 [4], Si [5] are also a reality. Differently from their carbon counterparts, BN nanotubes are always wide-gap semiconductor in character, with an energy band gap around 5.5 eV [6]. It turns BN nanotubes very attractive materials for nanoscale devices.

Many properties of semiconductor devices are derived from the presence of dopants in the otherwise pure materials. Hence, the possible implementations of nanotube-based devices require the study of suitable defects and impurities that could act as electron (or hole) donors/acceptors. First principle density functional calculations are nowadays recognized to provide accurate predictions of important structural and electronic characteristics of materials, serving as a reliable guide to experimental investigations. This is particularly true in the realm of structures in the nanometer scale.

Recently, theoretical investigations on neutral native defects and carbon substitutional impurities in BN nanotubes have been performed [7]. For all defects, localized levels appear deep in the gap and relatively low formation energies are obtained for the carbon substitutional impurities. The Si substitutional impurity in carbon nanotubes (Si_C) has recently been studied [8] and a relatively high formation energy of 3.13 eV was calculated. Furthermore, the possible role played by this defect in the control of the electronic doping characteristics of semiconductor carbon nanotubes against the adsorption of different foreign atoms at the Si impurity site have been investigated [9]. The amazing electronic flexibility predicted by these Si doped C nanotubes and the similarities between BN and C compounds leads to the natural question about Si impurities in BN nanotubes.

In this work a first principle study of neutral Si substitutional impurities in BN nanotubes is presented. It is shown that the incorporation of a Si atom in a B site has relatively low formation energy and that the electronic band structure of this defect is very similar to the case when a ligand X binds to the Si substitutional atom in a semiconductor carbon nanotube [9].

2 Methods

Self-consistent first principle large unit cell calculations based on the density functional theory are employed to the study of the Si substitutional atom in the B (Si_B) and the N (Si_N) sites of a (10,0) BN nanotube [10]. The local spin density approximation to the exchange and correlation functional as parameterized by Perdew and Zunger [11] is used. The interaction between ionic cores and valence electrons is described by norm-conserving pseudopotentials [12] in the Kleinamn-Bylander form [13]. The valence wave functions are represented by a linear combination of double-zeta pseudoatomic orbitals [14] and a cutoff of 80 Ry is employed to represent the charge density. The

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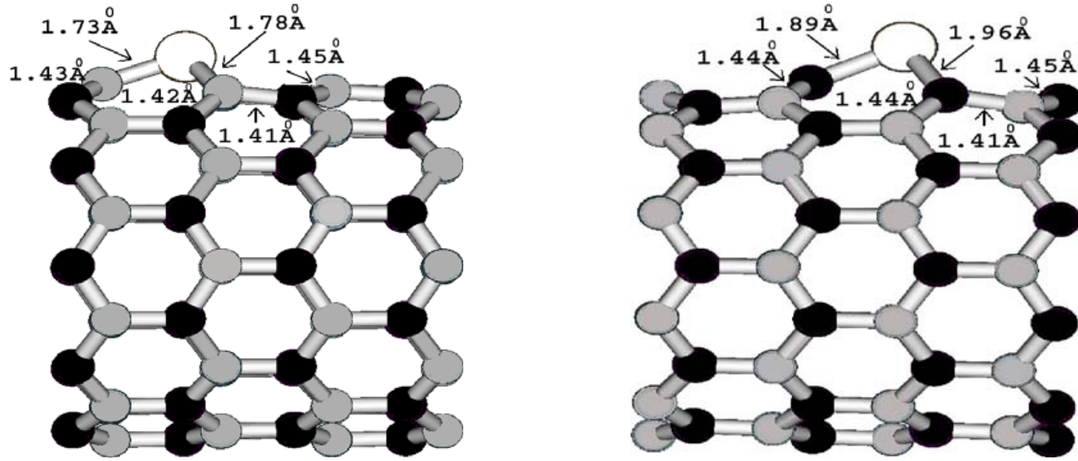

Fig. 1. Schematic representation of the (a) Si_B and (b) Si_N relaxed structures. The grey, black and white balls represent the N, B and Si atoms, respectively.

Brillouin zone is sampled with four k-points along the Γ-X direction [15].

The unit cell has 80 atoms of a zig-zag (10,0) BN nanotube. The atomic positions of the nanotube are fully relaxed until all the force components are smaller than 0.05 eV/Å. The Si atom is then incorporated as a substitutional atom in the tube and a new fully relaxation is performed. In order to assure that tubes in neighboring cells do not interact, the supercell dimensions in directions perpendicular to the tube axis are taken as 15.0 Å.

3 Results and discussion

The Figure 1a shows the resulting optimized structure of the (10,0) BN nanotube with a Si substitutional atom in a B site. A clear outward radial bump of 0.85 Å of the Si atom is observed. The distances between the Si atom and its first N neighbors are 1.73 Å, for the Si-N distance collinear with the tube axis, and 1.78 Å, for the two N atoms related by the mirror plane containing the Si atom and tube axis. As compared to the Si-N distances in β-Si_3N_4, where these distances vary from 1.71 Å to 1.76 Å [16], a very small enlargement is observed.

The band structure for the Si_B system is shown in Figure 2b. A singly occupied level appears 1.57 eV above the top of the valence band, in the gap region. This localized level is centered on the Si atom, as can be seen in Figure 3a. The band structures for electrons with spin up and down present no difference, the net spin of Si_B being zero. The singly occupied level in the gap region has an occupation of half electron for each spin components. Similarly to the results when a ligand atom binds to the Si substitutional impurity in a semiconductor C nanotube [9], this level at the gap region crosses the Fermi energy. This Si_B band structure can be easily interpreted. Three covalent Si-N bonds between the Si atom and its N first neighbors are formed and the localized additional electron coming from the Si atom appears in the gap region. Apart this level in the gap, the tube band structure remains almost unaltered, even with the significant relaxation of the system.

The formation energy, E_f, of the Si_B is calculated through the following formula

$$E_f[\mathrm{Si_B}] = E_t[\mathrm{Si_B}] - n_\mathrm{N}\mu_\mathrm{N} - n_\mathrm{B}\mu_\mathrm{B} - \mu_\mathrm{Si} \tag{1}$$

where $E_t[\mathrm{Si_B}]$ is the total energy for Si_B, n_X is the number of atoms of species X and μ_X is the chemical potential for species X. The chemical potentials for the B and N atoms must also obey the equilibrium condition [17],

$$\mu_\mathrm{B} + \mu_\mathrm{N} = \mu_\mathrm{BN}^{tube}. \tag{2}$$

The chemical potentials for B, N and Si are calculated as the total energy per atom of the hexagonal bulk B, the N_2 molecule and the bulk silicon, respectively. The μ_BN^{tube} is calculated as the energy per BN pairs of atoms in the tube. All these calculations are performed using the same calculational procedure as employed to the study of the Si substitutional impurities. Two extreme conditions can be identified, N-rich and B-rich environments. For a N-rich situation, the N chemical potential is that coming from the N_2 calculation whereas the B chemical potential is fixed through the equation 2 above. For a B-rich condition, on the other hand, the μ_B is taken as that derived from the bulk calculation, with the μ_N fixed according to equation (2).

From the calculated values for the formation energies shown in Table 1, one can see that, under N-rich conditions, the Si_B is likely to be present in the BN tube. For B-rich conditions, on the other hand, a value of 4.89 eV is obtained, which turns this defect practically absent in the tube, at least in the neutral charge state.

The relaxed structural configuration of the Si_N system is shown in Figure 1b. The Si atom presents an outward displacement of 1.33 Å, which is larger than the equivalent relaxation in the Si_B and around the double of that found in similar calculations for Si_C in carbon nanotubes [8]. The distances between the Si and its first neighbors are 1.89 Å, for the Si-B distance along the tube axis, and 1.98 Å, for

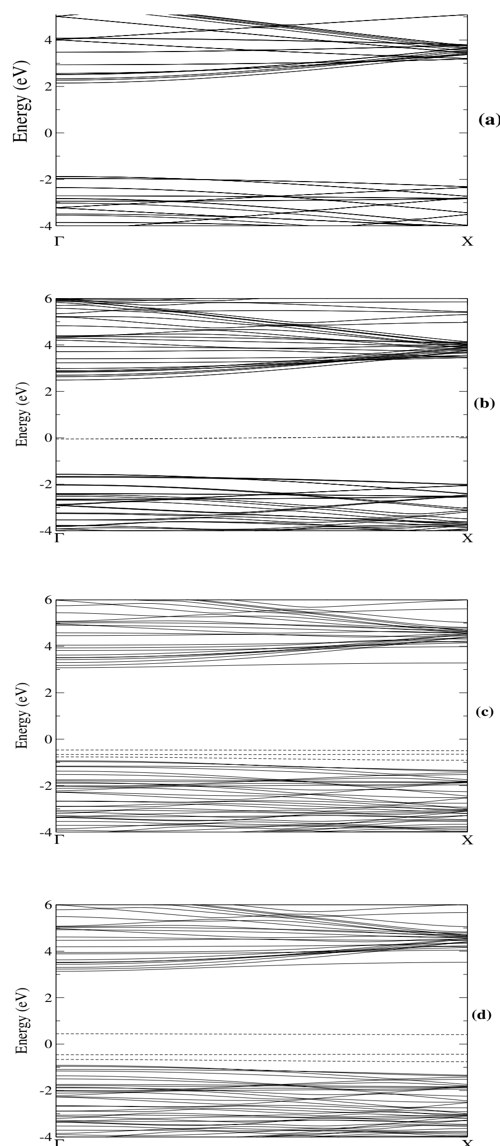

Fig. 2. Calculated band structures for (a) the (10,0) BN nanotube, (b) Si_B defect, (c) spin-up and (d) spin-down electrons for the Si_N defect. The dashed lines represent Si-derived levels. The Fermi energy is at zero eV.

Table 1. Calculated formation energies (in eV) for Si_B and Si_N in N-rich and B-rich conditions.

Defect	N-rich	B-rich
Si_B	0.50	4.89
Si_N	10.14	5.75

the other two Si-B distances. These Si-B distance values resemble those found in theoretical calculations for $SiBH_5$ isomers [18] and are a little larger than those for the silicon tetraboride (SiB_4) [16].

The spin-up and spin-down band structures for the Si_N system are shown in Figures 2c and 2d, respectively. The localized levels near the top of the valence band in the gap region are all centered on the Si impurity atom. The translational symmetry breaking introduced by the different potential wells of Si and N atoms leads to the detachment of the Si valence levels from the top of the valence band. A comparison between the band structures for fully relaxed and completely unrelaxed Si_N calculations shows that the localized nature and the position of these Si levels in the gap are only slightly dependent of the structural relaxation. The unoccupied spin down level is 1.37 eV above the top of the valence band and 0.44 eV above the Fermi energy. The highest occupied spin up level is 0.46 eV above the top of the valence band. The calculated exchange splitting between the lowest unoccupied and the highest occupied Si levels is of 0.46 eV.

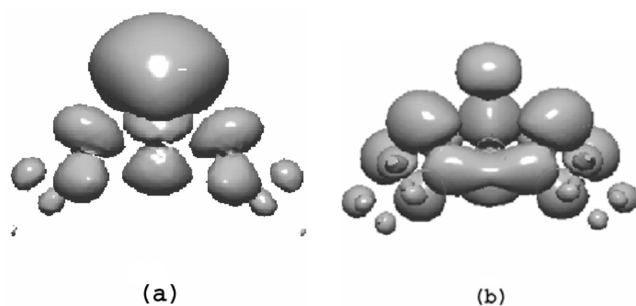

Fig. 3. Charge density plots for (a) the level at the Fermi energy for the Si_B and (b) the level at the bottom of the conduction band for the Si_N.

A charge density plot of the localized level at the bottom of the conduction band is shown in Figure 3b. This level has great contributions from the three first neighbors B atoms. A comparison with the non-relaxed calculation shows that this level localizes due to the outward displacement of the Si atom, presenting a tube-like dispersion before the relaxation.

It is interesting to compare the band structures of the Si_N defect with that for the Si_C defect in a semiconductor carbon nanotube [9]. Similarly to the Si_N in the BN nanotube, the Si_C shows an unoccupied Si level in the gap region. With the adsorption of foreign atom at the Si impurity site, this Si based level turns resonant in the valence band and a nearly delocalized tube level appears in the gap crossing the Fermi energy. A similar behavior could also be explored for this Si_N defect in BN nanotubes.

The formation energies for the Si_N defect at N-rich and B-rich conditions are shown in Table 1. The calculated values for Si_N are much higher than those for Si_B and practically inhibit the presence of neutral Si_N defects. However, the presence of the unoccupied level deep in the gap region opens the possibility that negatively charged states of the Si_N defect could have lower formation energies and be present in the system.

Considering the band gap as the difference in energy between the delocalized tube-like states at the bottom of the conduction band and the top valence band, it is seen that the defective systems alter the (10,0) BN nanotube gap of 4.03 eV only by additional 20 meV. Nevertheless,

the presence of defective levels in the band gap completely changes the optical and electronic behaviors of these systems. The band structure of the low formation energy Si_B defect turns it, in principle, possible to be identified by optical experiments once transitions from the level in the gap should require much lower energies than the nanotube intrinsic transitions.

4 Conclusions

A first principles study of neutral Si substitutional impurities in a (10,0) BN nanotube has been performed. For both possibilities, Si_B and Si_N, significant outward radial relaxations of the Si atom are observed, resulting in Si-first neighbors distances similar to those found in silicon compounds involving B and N atoms, respectively. For the Si_B case, the band structure shows a level crossing the Fermi energy centered on the Si impurity atom and no spin polarization is determined. For the Si_N defect a split between up and down levels of the Si atom is calculated and the Si levels appear in the gap region. The localization of these Si levels is a consequence only of the difference of the Si and N potential wells, being independent of the structural relaxation of the system. The nearly localized level at the bottom of the conduction band for the Si_N defect is located on the B first-neighbors. The calculated formation energies for N-rich conditions show that the neutral Si_B is likely to be present, with the other neutral defects presenting much higher formation energies.

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