Band structure of boron doped carbon nanotubes

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Abstract. We present *ab initio* and self-consistent tight-binding calculations on the band structure of single wall semiconducting carbon nanotubes with high degrees (up to 25 %) of boron substitution. Besides a lowering of the Fermi energy into the valence band, a regular, periodic distribution of the p-dopants leads to the formation of a dispersive "acceptor"-like band in the band gap of the undoped tube. This comes from the superposition of acceptor levels at the boron atoms with the delocalized carbon π-orbitals. Irregular (random) boron-doping leads to a high concentration of hybrids of acceptor and unoccupied carbon states above the Fermi edge.

INTRODUCTION

The electronic properties of single wall carbon nanotubes depend sensitively on the diameter and the chirality of the tubes. Therefore, in order to use tubes as elements in nano-electronical devices, a controlled way to produce and separate a large quantity of tubes of specific radius and chirality has to be found. Alternatively, doping of tubes by boron and nitrogen [1] may lead to electronic properties that are more controlled by the chemistry (i.e., the amount of doping) than the specific geometry of the tubes. Indeed, theoretical investigations of BCN nanotube heterojunctions have predicted that the characteristics of these junctions are largely independent of geometrical parameters [2]. It has been predicted that even stochastic doping may lead to useful electronic elements such as chains of random quantum dots and nanoscale diodes in series [3].

The realization of p-type doping of pure carbon nanotubes by a substitution reaction with boron atoms [4, 5, 6] offered the possibility to transform semiconducting tubes into metallic tubes by lowering the Fermi level into the valence band. Indeed, transport measurements [7, 8, 9] have shown a clearly enhanced conductivity of B-doped tubes. The metallic behavior of B-doped multiwall carbon nanotubes was also confirmed by scanning tunneling spectroscopy [10].

In bulk semiconductors, typical doping concentrations of impurity atoms are around 10^{-3} %. At such low concentration, the presence of group III atoms (e.g., B) in a group IV semiconductor leads to the formation of an acceptor state (non-dispersive band) in the band gap at low energy above the valence band edge [11]. For B doping in a C(8,0) tube, Yi and Bernholc [12] have calculated (using a B/C ratio of 1/80) that this acceptor state is located at 0.16 eV above the Fermi energy. However no discussion has been made up-to-date on the evolution of this acceptor-like level with the degree of B-doping. Since in recent experiments [6], Boron substitution up to 15 % has been reported, we investigate in this paper the band structure of strongly B-doped single wall carbon nanotubes.

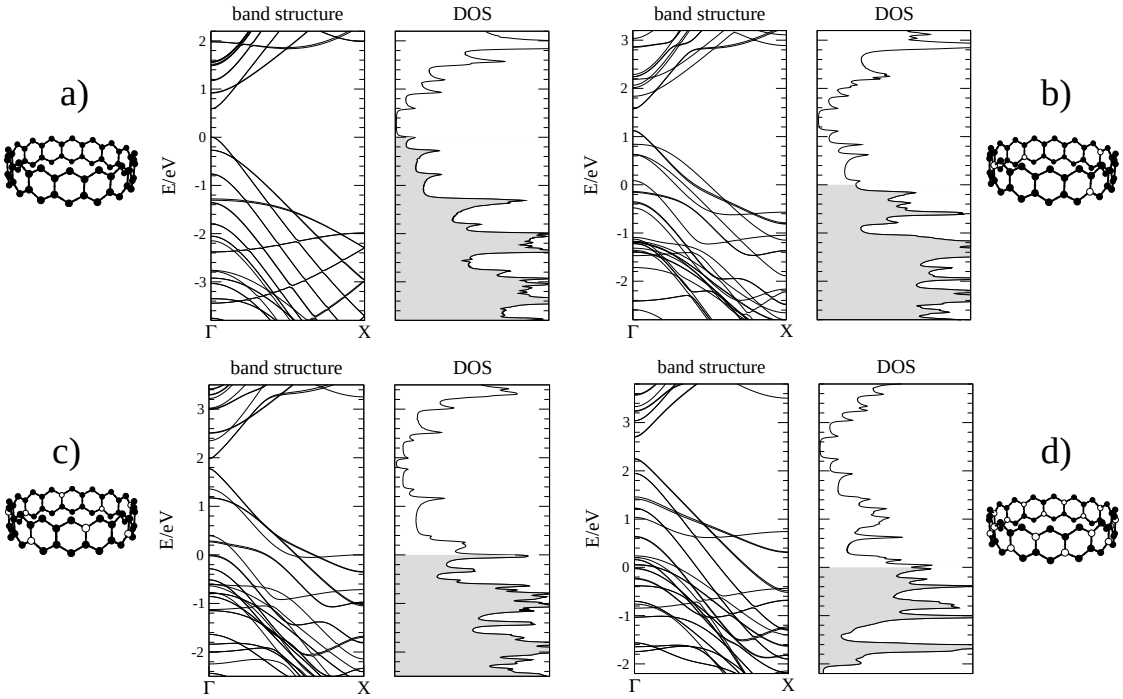

FIGURE 1. Band structure and DOS of a C(16,0) tube with a) 0%, b) 6.25%, c) 12.5%, and d) 25% boron doping. Zero energy denotes the Fermi edge. Filled states are indicated by grey shadowing. Insets display the corresponding unit cells (C atoms black, B atoms white).

COMPUTATIONAL METHOD

In order to demonstrate the effect of B doping on a semiconducting tube, we have chosen a (16,0) tube with a diameter of 12.5 Å which is close to the average radius of commonly produced SWNT samples. Since the distribution of borons in B-doped tubes is still unknown, we have performed two sets of calculations. 1.) For regular periodic distributions that are commensurate with the unit-cell of the undoped tubes, we perform *ab initio* calculations [13] of electronic band structure and density of states (DOS). 2.) In order to test the effect of disordered B doping, we employ a supercell comprising 6 unit-cells (384 atoms) and distribute the boron atoms “randomly” with the only constraint that they cannot occupy nearest neighbor positions on the hexagonal carbon grid. For this large system, we use a self-consistent tight-binding (SCTB) method [3, 15].

RESULTS

Fig. 1 shows the band structure and DOS of a C(16,0) tube without doping and with various concentrations of B-doping in a periodic manner (see insets). For the undoped tube it can be noted, that the DOS is symmetric around the band gap for the 1st and 2nd Van-Hove singularities (VHSs). However, beyond this small energy regime around the band gap, asymmetries arise due to the mixing of p and s orbitals. Doping of the tubes

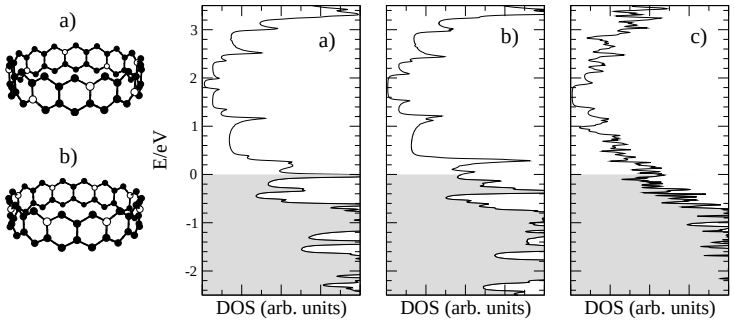

FIGURE 2. DOS of a C(16,0) tube with 12.5% B doping: a) regular doping (as in Fig. 1), b) regular doping (alternative geometry, c) random doping.

leads to a lowering of the Fermi level into the valence band of the undoped tube. Clearly, the stronger the doping, the stronger is also the shift of the Fermi level. Above the highest occupied bands of the undoped tube new bands are formed. These bands correspond to the formation of an acceptor level in semiconductors with very low dopant concentration. Due to the strong concentration in the present case, the boron levels hybridize with the carbon levels and form strongly dispersive "acceptor-like bands". The band structure of the valence band is strongly distorted upon doping, because the levels of carbon atoms that are substituted by boron move upwards in energy. In addition, the lowering of the symmetry by doping leads to many clear avoided crossings between states that perform a real crossing in the case of the undoped tube where they posses a different symmetry. Clearly, in all cases displayed in Fig. 1, the doping with B leads to a metallic character of the tube. However, the density of states at the Fermi level strongly depends on the geometry of the structure and varies non-monotonously with the doping concentration. In fact, in BC_3 tubes with a different geometry than in Fig. 1 d), a gap between π-type orbitals and σ type orbitals opens up at the Fermi level and renders the tubes semiconducting in this particular case [17].

Fig. 2 compares the DOS of a C(16,0) tube with 12.5% boron substitution in three different geometries. The two regular structures both display a pattern with the familiar pronounced Van Hove singularities of a 1-dim. band structure. However, the different ordering of the boron atoms gives rise to a different hybridization of the bands and thereby to a pronounced difference in the peak structure of the DOS. The DOS at the Fermi level strongly depends on the ordering of the B atoms. In the DOS of the randomly doped tube, the pattern of the VHSs is mostly smeared out [18]. Due to the missing translational geometry, the 1-dim. band structure of the regularly doped tubes is transformed into the DOS of a 0-dimensional structure, i.e. of a large molecule or cluster without periodicity. The states between the Fermi level and the original valence band edge of the undoped tubes are hybrids of acceptor levels and unoccupied carbon levels. The electronic excitations into these levels should explain the optical absorption spectra of B-doped carbon tubes [6]: In addition to the pronounced absorption peaks that are commonly affiliated with the transitions E_{ii} $(i = 1,2)$ from the first/second occupied VHS to the first/second unoccupied VHS of the pure semiconducting carbon tubes, the spectra of B-doped tubes display additional absorption at energies lower than E_{11}.

CONCLUSION

The calculations on the band structure of boron doped carbon nanotubes clearly confirm the expectation (and experimental observation) that these tubes are metallic with low resistance. For regularly doped structures, we have observed the formation of a dispersive "acceptor" band while the Fermi level is shifted downwards into the valence band of the undoped tubes. Electronic excitations into these hybrids of acceptor states and unoccupied carbon levels are expected to play an important role in optical absorption spectra. Randomly doped tubes display the same downshift of the Fermi edge but cease to display strongly dispersive bands. We hope that in the near future, spatially resolved TEM/EELS will help to elucidate the exact geometry of the boron dopants and scanning tunneling spectroscopy will probe the exact density of states.

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13. The *ab initio* calculations have been performed with the code ABINIT, using density-functional theory (DFT) in the local density approximation (LDA). We use a plane wave expansion with an energy cutoff at 50 Ry. Core electrons are simulated by Troullier-Martins pseudopotentials. A supercell geometry is employed with a large inter-tube distance (10 a.u.). The density is calculated self-consistently using a sampling of 8 k-points for the (quasi-one dimensional) first Brillouin zone of the tubes. A non-self consistent calculation yields the energies of occupied and unoccupied states on a grid of 50 k-points. Since the tubes have large diameter, we have neglected the effect of local atomic distortion induced by doping which leads to a small outward movement of the boron atoms (< 0.11 Å [12]).
14. The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (URL http://www.abinit.org).
15. In the SCTB calculation (following Ref. [3]) we use a non-orthogonal tight-binding basis with s and p valence orbitals, fitted to LDA calculations [16]. The Coulomb potential generated by the charge density is self-consistently included as a shift in the on-site potentials. We have checked for the systems displayed in Fig. 1 that the SCTB yields results in very close agreement with the *ab initio* calculations.
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18. The system still possesses a translational symmetry even though with a large unit cell. Therefore, some of the dispersive band structure, including Van-Hove singularities, is still visible.