

Effects of Nanodomain Formation on the Electronic Structure of Doped Carbon Nanotubes

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Changes in the electronic structure of multiwalled nanotubes due to the introduction of boron in the lattice are identified using scanning tunneling spectroscopy. Doped tubes are metallic with no apparent band gap, in contrast to undoped tubes with varying electronic character. Combined with *ab initio* calculations, we show that changes in the local density of states, as determined from tunneling spectroscopy, must be interpreted in terms of nanodomains of dopant islands and not as isolated substitutional species. [S0031-9007(98)07103-8]

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Generally, property modification through doping is difficult when device dimensions are submicron. This comes from the enormous stresses within ultrasmall structures and electromigration during use, both of which drive segregation of the dopants [1]. Carbon nanotubes may offer the possibility of realizing carbon based nano-electronic components which circumvent some of these difficulties [2].

Single-walled nanotubes (SWNT's), single graphene cylinders, and multiwalled nanotubes (MWNT's), coaxial graphene cylinders, are now routinely produced [3,4]. Current flow is mediated by the π - π^* bonding of the sp^2 hybrids, as in graphite, and thus the tube is intrinsically two dimensional. The topology of a nanotube, its diameter, chirality, and defect structure, is strongly coupled with its electronic properties. This has led to the idea of constructing nanoelectronic devices by joining carbon nanotubes of different topologies and hence electronic properties [5]. While an interesting possibility, at present this cannot be performed in a controllable fashion. Moreover, the geometry of nanotubes is altered by the introduction of topological defects, clearly undesirable if they are to be used as device elements.

The introduction of donor/acceptor levels through substitutional doping of the material seems an attractive alternative for control of electronic properties. Theoretical studies have suggested that electronic devices can be based on composite $B_xC_yN_z$ nanotube heterojunctions [6]. Recently several groups have succeeded in synthesizing doped carbon nanotubes, or tubes with a $B_xC_yN_z$ composition, in the arc discharge [7-9] and by gas-phase pyrolysis [10]. In this Letter we show for the first time direct measurements of the local electronic properties of B-doped carbon nanotubes and demonstrate

the feasibility of nanoheterojunctions through substitutional doping.

Doping was carried out by growing tubes in a carbon arc using a BN-rich consumable anode as discussed in earlier publications [8,11]. Boron concentrations of individual doped nanotubes were of the order of 1 to 5 at. % as determined from analytical transmission electron microscopy [8], with little N (<1 at. %), though N is present during synthesis conditions. This differs from recent arc methods where a boron containing HfB_2 anode is arced against a graphite cathode in a nitrogen atmosphere [9]. The latter produced composite structures of BN and C layers suggesting complete phase separation between BN and C three dimensionally. Our results show a two-dimensional segregation of B into nanodomains within the carbon layers of the nanotube, especially the outermost layers [8]. Nitrogen is released when the anode of composite BC_2N stoichiometry is broken down in the arc. Similar results are obtained for composite anodes of graphite and amorphous boron [8]. For scanning tunneling microscopy (STM) and spectroscopy (STS), pure or doped nanotubes were dispersed in ethanol and dried onto cleaved highly oriented pyrolytic graphite (HOPG) substrates. STM and STS [12] were carried out in UHV (< 10^{-9} Torr). Tunneling tips were mechanically formed Pt-Ir.

Figure 1 is a $2 \mu m \times 2 \mu m$ constant current image of an isolated B-doped carbon nanotube. At the bottom of the image are two steps on the HOPG substrate of unit cell height each. To ensure that the image is that of a nanotube and not of one of the many anomalous defects known to be present in HOPG, the tube was moved using the tip of the STM. Further, the tube is observed to be continuous across the HOPG step edges, implying that

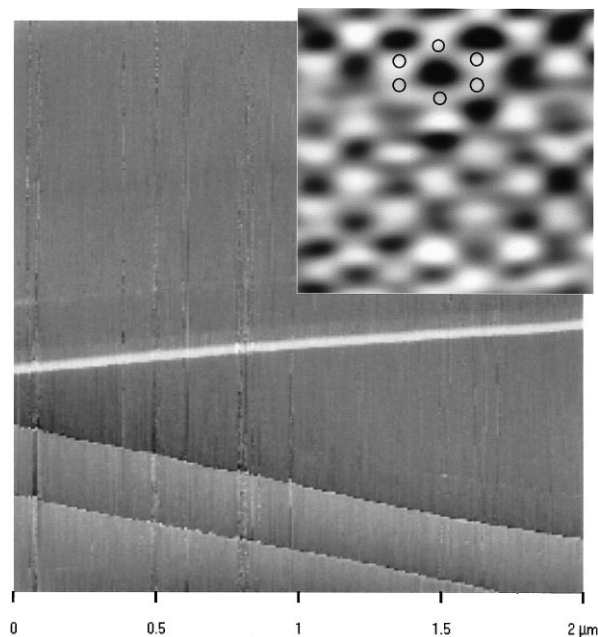


FIG. 1. An STM image of a isolated B-doped nanotube (acquired at 50 meV at 0.15 nA). The tube diameter is approximately 20 nm as determined from the tube height in the image; its width appears larger due to tip convolution. The inset image has been “flattened” by the imaging process, causing a slight distortion of the hexagonal symmetry of the lattice.

it lies on top of them. The inset is a $0.1 \text{ nm} \times 0.1 \text{ nm}$ enlargement of the tube body, showing atomic scale corrugations. It is shown with the axis of the tube in both images aligned. While the flattened presentation of the curved surface has resulted in slight distortions of the hexagonal symmetry in the atomic structure, it still suggests that this tube has an “armchair” configuration (shown schematically by the black circles). There is little difference in the overall morphologies of pure and doped tubes, with the exception that the doped tubes are extremely long, usually exceeding the scan range of the microscope.

Figure 2(a) compares representative local density of states (LDOS) near the Fermi level, as derived from tunneling spectra [12], of isolated, doped, and pure nanotubes. In both cases the spectra were acquired on tube bodies of 20 nm in diameter, and spatially removed from the influence of tube tip states [13]. The closing of the “apparent band gap” in doped tubes and the development of a prominent acceptorlike feature on the valence band side close to the Fermi level is striking and was observed in all of the roughly 40 examples studied. This band edges of the undoped tube show no evidence of the state found in the doped samples. The acceptorlike peak is narrower in energy than the other features seen in the LDOS of the tubes. While different undoped tubes exhibit a range of electronic structures (depending on diameter and chirality), this sharp acceptorlike feature

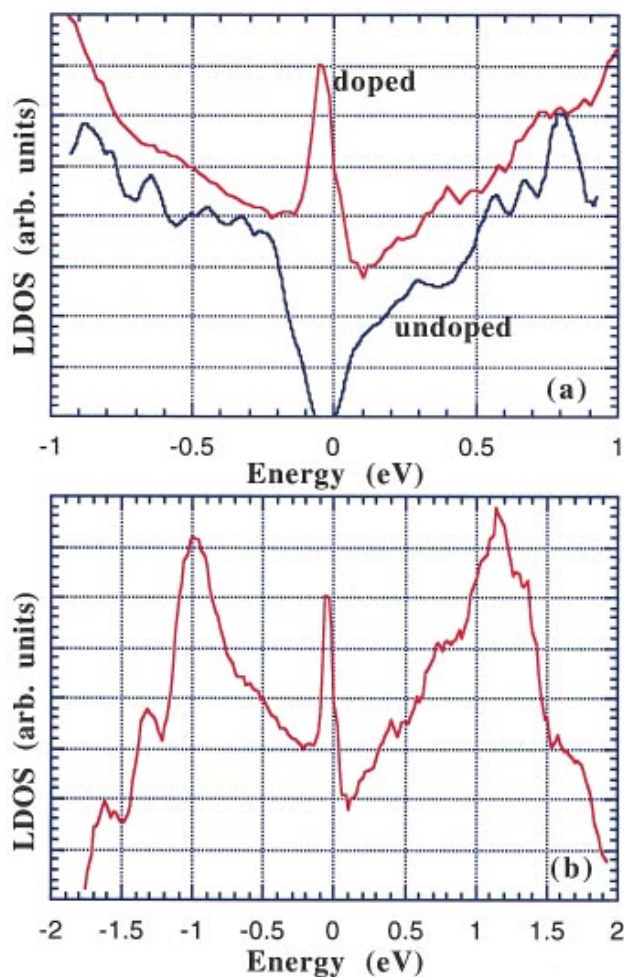


FIG. 2(color). (a) The LDOS of doped (top) and pure (bottom) carbon nanotubes are compared. Doping has led to a prominent acceptorlike feature near the Fermi level. (b) At energies far from the Fermi energy, large singular structures occur in the LDOS.

is never seen on undoped tube bodies. We have found similar resonance features at the tips of pure carbon nanotubes related to the presence of fivefold rings [13].

In Fig. 2(b) the existence of singularities in the LDOS is shown for energies far from the Fermi level (the large enveloping features at approximately $\pm 1 \text{ V}$). They are equispaced with respect to the Fermi level as would be expected from Van Hove type singularities in a two-dimensional, σ , or π -bonded system [14]. Singularities in the density of states of pure single shell tubes have been observed recently and show clear differences between metallic and semiconducting tubes [15]. The observation of singular points in the doped samples is indicative of an exceptionally high structural perfection in the outermost tube cylinders probed by the STS measurements. For such systems, the prominent (single) acceptorlike peak close to the Fermi level cannot be associated with the onset of carbon-related Van Hove type singularities [15] as they would occur in symmetric pairs.

Theoretical studies have predicted sharp acceptor states related to B doping in carbon nanotubes 0.16 eV above the top of the valence bands [16]. However, these calculations have been performed for larger band gap, semiconducting nanotubes (chiral and small diameter) and are not directly applicable here. As shown in Fig. 1, the tunneling spectra used to derive the LDOS in Fig. 2(b) was acquired from what is likely to be an armchair tube which is relatively large in diameter, implying it to be metallic or a semimetal. We have performed *ab initio* band structure calculations of B- and N-doped graphitic systems within the local density approximation to the density function theory [17]. We adopt first a 3×3 graphite unit cell and replace one of the 18 C atoms by a B atom, leading therefore to an $\sim 5.5\%$ substitutional doping. The main effect of B substitution on the graphitic DOS is to lower the Fermi level by as much as ~ 1.2 eV [18]. Beyond this effect, and as compared to pure graphite, we did not observe any significant modification of the π band's DOS. B-related acceptor states could only be detected in the σ bands, that is, at much lower energy than the experimental value for the strong acceptor state observed in Fig. 2 [19]. We obtain similar results for N substitutional doping (or BN substitution of C_2 dimers).

These results lead to the conclusion that the metalization and the strong "acceptor" state observed by experiment cannot be explained by isolated B (or N) substitutional atoms in the graphite network. As a simple variant to this model we assume segregated islands of stoichiometric BC_3 composition in metallic carbon nanotubes. With increasing diameter, the local electronic properties of the islands rapidly recover those of the infinite BC_3 sheet [6]. The DOS associated with the islands is shifted in energy with respect to the DOS of graphite in order to align the Fermi levels, with the shift being directly related to the island size. As a consequence, the "segregation" of B into small BC_3 -like islands does not result so much in lowering the Fermi level of the host carbon nanotube (as in the case of isolated B atoms), but leads rather to the superposition of both the DOS of the carbon nanotube and of the BC_3 islands after Fermi level alignment. Thereby, the DOS of BC_3 is "shifted up" in energy with respect to its carbon nanotube substrate, resulting in the presence of the strong BC_3 -related π peak just below the Fermi level of the original, undoped carbon nanotube. This is illustrated in Fig. 3 where we plot the DOS associated with a 10 Å BC_3 island embedded in a metallic (6,6) nanotube. The obtained composite (island + tube) LDOS exhibits peaks in good agreement with the experimentally determined peak positions for doped tubes (Fig. 2) [20]. We note that similar results can be obtained in the case of BN - or BC_2N -like islands presenting an excess of B atoms.

The acceptorlike state suggesting "metallic" character, as well as the singularities, are common to all STS measurements performed on doped nanotubes. This is ex-

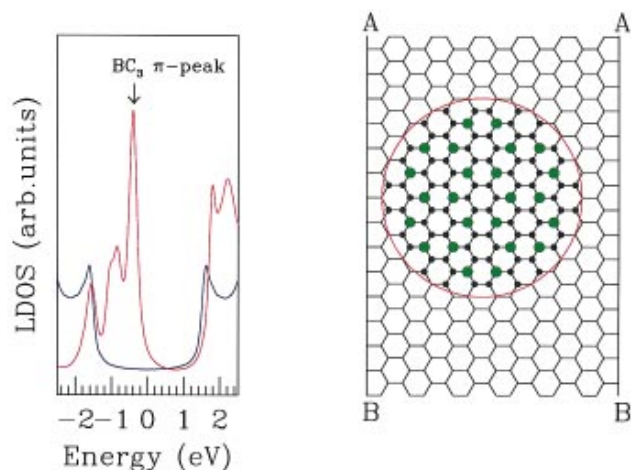


FIG. 3(color). The theoretical LDOS associated with a BC_3 island (encircled region) plotted with the LDOS associated with a pure carbon island of the same radius, located far away from the B atoms as depicted in the unfolded tube model to the right (to reform the tube A has to be joined with A' and B with B' , respectively). We use here a simple tight-binding recursion approach which allows the study large systems and has been shown in Ref. [6] to capture the essential features associated with composite $B_xC_yN_z$ nanotube heterojunctions. The LDOS of the two areas are expected to be superimposed on each other in the experimental measurements.

pected. If we take islands of the kind represented in Fig. 3 arranged hexagonally on the tube, a straightforward estimate shows the average island-to-island distance (center-to-center) to be 4.0 nm, giving a doping level of 5%. Thus, the maximum distance from an island in the doped nanotube is 1.3 nm, only a few bonds away. Further, our model implies that the peak position is determined by the total electronic charge transfer to the island (island size) and not where the tip is in relationship to the island. In these experiments, the individual islands were not directly imaged. For stable atomic scale imaging positive voltages were used, and the acceptor peak (which would lead to enhanced contrast near the islands) is at negative voltages. However, as demonstrated in Fig. 4, there are variations in the tunneling spectra along a single tube which suggest island formation. Figure 4(a) compares the LDOS around a single point on the tube with the tip positions only a few nanometers apart. These spectra represent the LDOS of a single island with the tip at two different distances from the island. The lower curve was taken further away from the island, and a corresponding decrease in peak intensity is observed. In Fig. 4(b) the LDOS near two different islands (with presumably different sizes) are compared and different positions are observed for the acceptorlike feature. We note that such local LDOS variants will also reflect the existence of different nanodomain structures and compositions.

In conclusion, using tunneling spectroscopy we were able to demonstrate that B-doping of carbon nanotubes

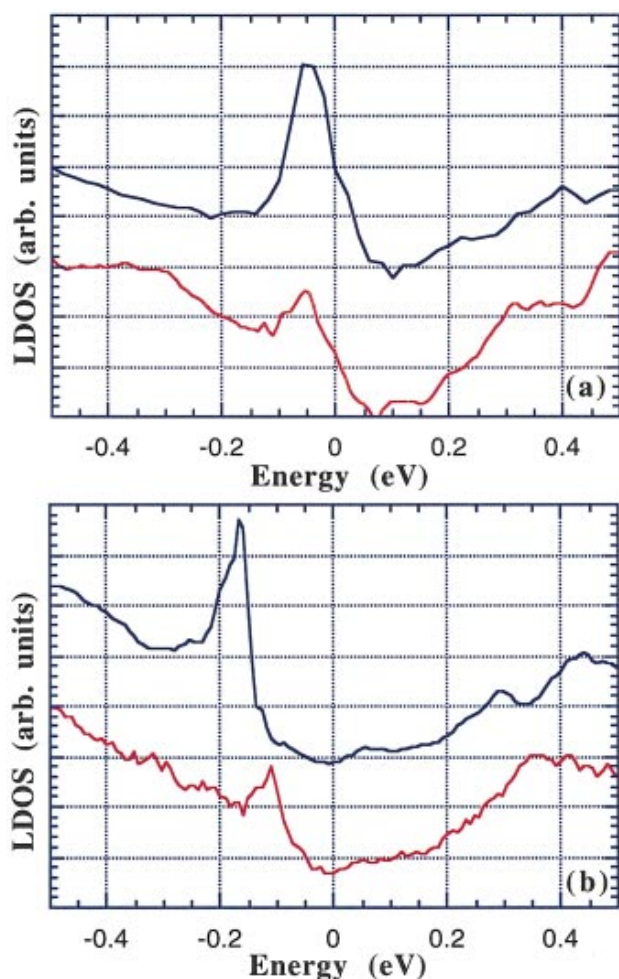


FIG. 4(color). (a) A comparison of the variations of the LDOS associated with specific area, and thus a specific island, shows a decrease in the peak intensity as the tip is positioned away from the island. (b) At different spatial positions on the tube, and thus near islands of different size, the acceptorlike state exhibits marked differences in peak position. The curves have been offset vertically for clarity.

results in the introduction of a prominent acceptorlike state very near the Fermi level of the material. Calculations suggest that the prominent central acceptorlike feature in the LDOS can be interpreted as resulting from nanodomains of BC_3 within the metallic nanotube lattice.

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