Stochastic Heterostructures and Diodium in B/N-Doped Carbon Nanotubes

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Carbon nanotubes are one dimensional and very narrow. These obvious facts imply that, under doping with boron and nitrogen, microscopic doping inhomogeneity is much more important than for bulk semiconductors. We consider the possibility of exploiting such fluctuations to create interesting devices. Using the self-consistent tight-binding technique, we study heavily doped highly compensated nanotubes, revealing the spontaneous formation of structures resembling chains of random quantum dots, or nanoscale diodelike elements in series. We also consider truly isolated impurities, revealing simple scaling properties of bound state sizes and energies.

The intrinsic transport properties of carbon nanotubes are promising for nanoelectronic applications, but useful intratube devices usually require electronic heterogeneity. Until now, experimenters have either imposed the requisite heterogeneity through electron-beam lithography on a much larger length scale (e.g., gate contacts, masked potassium doping [1]), or exploited preexisting inhomogeneities such as on-tube defects [2], chance placement of external nanoparticles, or tube-tube crossings [3]. One potential route to stable, small-scale heterogeneity of electronic properties is substitutional doping by boron and nitrogen. Such doping has already been achieved by a variety of techniques, including arc discharge [4], pyrolysis [5], chemical vapor deposition [6], and substitution reactions [7]. Spatial variation in dopant density is much more important in 1D nanotubes than in bulk semiconductors. Fluctuations are large and electrons cannot bypass anomalous regions. Normally, such fluctuations would be considered a nuisance or worse. We ask: Can they be exploited? After all, a heavily doped compensated nanotube is a chain of p-n junctions (which might be called "diodium"). We demonstrate the potential of the idea by studying the electronic structure of heavily doped ($\sim$1 at. %), highly compensated nanotubes.

This paper takes an atomic-level view of doping and junctionlike structures. Previously, large-scale inhomogeneous structures, i.e., Schottky barriers and p-n junctions, were investigated in continuum [8–10] and self-consistent virtual crystal [11] approximations, with an emphasis on the mesoscale electrostatic peculiarities of one-dimensional systems [8]. Such studies provide valuable insights, but cannot access properties arising from atomic-scale structure. *Ab initio* techniques, on the other hand, have been applied to a variety of microscopically ordered, homogeneous, nanotube materials: BN, BC_3, and BC_2N [12]; BC_{40} and NC_{40} [13], $C_{17}N$ [14], and abrupt C/BN junctions [15]. There is no previous theoretical study of genuinely randomly (i.e., realistically) doped and compensated nanotubes.

In a d-dimensional doped semiconductor, the typical fluctuation in total dopant charge in a region of linear size L is proportional to $L^{d/2}$ (assuming Gaussian statistics), leading to fluctuations in the unscreened Coulomb potential proportional to $L^{(d-2)/2}$. Only for $d = 1$ is the exponent $(d - 2)/2$ negative. This implies that the dominant fluctuations are then on the shortest length scale over which the system is genuinely one dimensional, i.e., the circumference. (If the doping is so low that the length per dopant [λ] exceeds the circumference, then λ is the dominant scale.) This contrasts with bulk materials, for which the most important fluctuations can be on very long length scales and are controlled by screening, especially for light doping and high compensation [16]. Screening is ineffective at short distances in nanotubes; taking screening into account merely strengthens the conclusion. We can estimate the potential fluctuation (ΔV) over an axial distance $L = 2\pi R$ by computing the average potential produced by a Gaussian ("$\sqrt{N}$") charge fluctuation. Denoting the proportion of atoms which are dopants by c, the dielectric constant by $\tilde{\epsilon}$ [17], and using the graphene lattice constant 2.45 Å, we find $\Delta V \approx 9$ eV $c^{1/2}/\tilde{\epsilon}$. This is consistent with the numerical results presented below. Note that ΔV is independent of R for fixed c. Fluctuations in the azimuthal locations of dopants are not important: All azimuthal Fourier components of the doping have the same variance, but the potential arising from nonuniform components [$m \neq 0$, see Eq. (1)] falls off rapidly and cannot be resolved by intraband processes. (Numerical results confirm that they have little effect.)

Ab initio methods are prohibitively expensive for large systems, and ordinary tight binding is unable to treat charge transfer over distances greater than about a bond length, so that we have chosen to use a self-consistent tight-binding (SCTB) technique. The nonorthogonal [18] tight-binding basis contains four orbitals per atom with Hamiltonian and overlap parametrization determined directly from density functional theory in the local density approximation (LDA) [19]. This parametrization was shown to give results in

good agreement with LDA over a wide range of structures with short-range charge transfer. We impose self-consistency of long-wavelength components of the Hartree Coulomb potential via an iterative procedure [20]. Figure 1 compares results of simple TB, self-consistent TB, and LDA for a strongly charge modulated planar structure. SCTB is remarkably effective at correcting the deficiencies of simple TB, reproducing the main band narrowing and shift of Fermi energy level crossing exhibited by the LDA calculation, and is therefore expected to describe the physics near E_F well. The data presented here are for mechanically unrelaxed systems. Tests show that relaxation introduces only minor corrections to the electronic structure.

A length of nanotube heavily doped with both boron and nitrogen might have a substitution pattern similar to that shown in the second panel of Fig. 2. This shows a section of $(8, 0)$ nanotube (cut open and rolled flat with the axial direction horizontal) containing a number of boron and nitrogen atoms substituted on randomly chosen sites. The section is treated as the unit cell of a superlattice. A more lightly doped sample is shown in Fig. 3. Fluctuations in the doping act as *collective impurities,* creating localized impurity states in the energy gap of the undoped nanotube. This localization is illustrated by the plots of the axial probability densities (azimuthal average of $|\psi|^2$) of deep collective donor and acceptor states. These states arise from a local imbalance in the dopant charge of only one or two unit charges. Regions with excess nitrogen atoms suppress the local density of states (DOS) near the bottom of the gap (vice versa for boron-rich regions). This remnant of band bending would matter little in a bulk material, but in a one-dimensional structure can effectively block charge transport if the Fermi level lies in such a local pseudogap.

These randomly doped nanotubes resemble disordered chains of tiny quantum wells or dots, and could show a variety of behaviors characteristic of such structures, e.g., negative differential resistance. Level spacing in the wells is $\Delta \sim 10^{-1}E_{\text{gap}}$. Bandwidths for the well states, $\Gamma \sim 1$ meV for the samples studied, measure interwell tunneling matrix elements. The charging energy scale, $E_C = e^2/(\tilde{\epsilon}2\pi R) = (0.64/\tilde{\epsilon})E_{\text{gap}}$, scales with the gap. This is a significant energy, so that one must remember the local DOS plots in the figures are specific for neutrality in the depicted unit cells. A length of compensated doped semiconducting tube, particularly under imperfect dopant mixing, forms a dense sequence of alternately directed nanoscale diodelike elements. Reverse-biased structures should dominate transport under a voltage; field doping the tube would wash out weaker junctions, isolating regions of most pronounced nonlinear behavior.

Leonard and Tersoff [8] provided a formula showing that the depletion layer of a nanotube p-n junction is very long at low doping, but shrinks exponentially with doping.
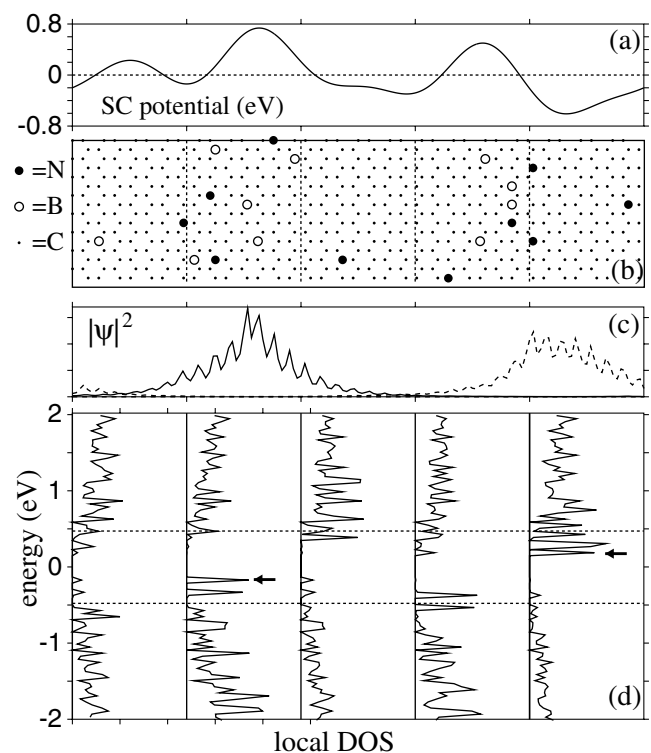
FIG. 2. SCTB results for sample A, an $(8, 0)$ nanotube randomly doped with ten each nitrogen and boron atoms per supercell of length 7.7 nm (overall doping level 3.5%). The horizontal direction in all figures corresponds to the axial direction. (a) Azimuthally averaged self-consistent potential. (b) The doping pattern in the unit cell cut open and laid flat. (c) Axial probability density profiles of deep donor and acceptor states (marked by arrows in the density of states plots). (d) Total densities of states for the corresponding slices indicated by dashed lines in panel (b). Dashed lines show the gap edges of an undoped $(8, 0)$ nanotube (centered at zero).
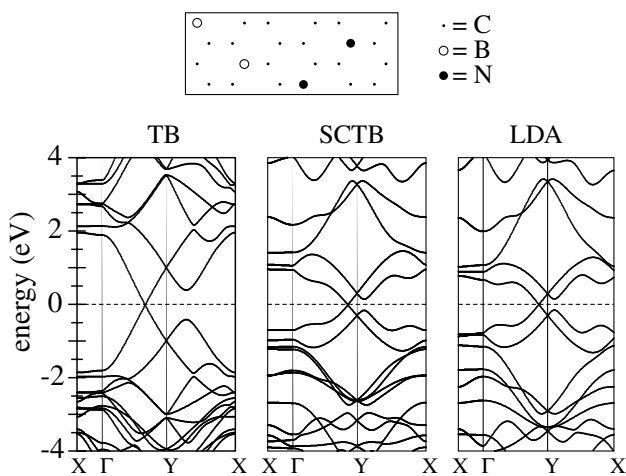

FIG. 1. Test of SCTB against LDA on a regular planar $BC_{10}N$ structure. Top: Unit cell. Bottom: Electronic energy bands near the Fermi level (dashed line) calculated by simple TB, SCTB, and LDA-DFT.
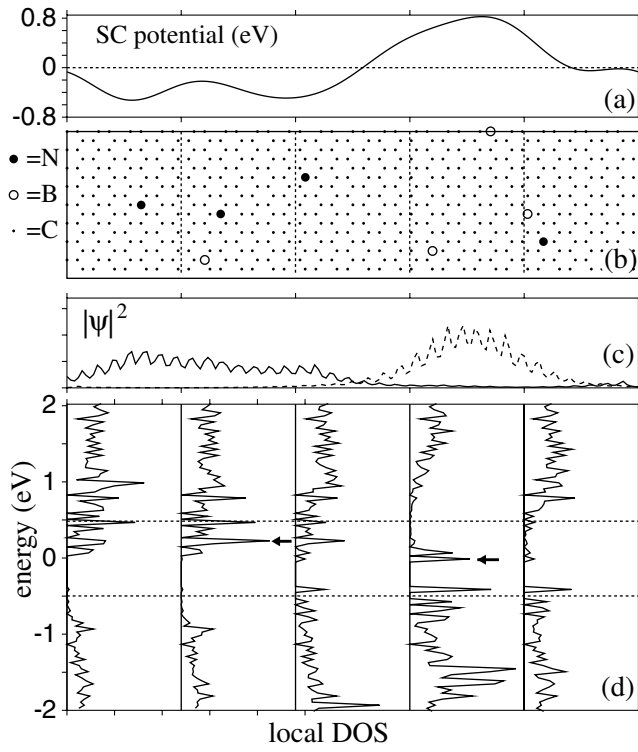
FIG. 3. Sample B: SCTB results for an $(8, 0)$ nanotube with a better segregated and lower density arrangement than sample A, containing four each nitrogen and boron atoms per 7.7 nm unit cell. Presentation is as in Fig. 2.

FIG. 4. Sample C: SCTB results for a doped $(6, 6)$ nanotube (6.9 nm unit cell) with 1.2% each boron and nitrogen. The dashed lines, centered at zero, indicate the edges of the $m = \pm 1$ subbands of the undoped tube, at which the DOS jumps suddenly from a low constant value.

Unfortunately, the formula is not applicable to the high doping ($\sim 1\%$) regime relevant to devices with nanometer-scale structure. The depletion width in sample B is close to being saturated and is very narrow (~ 1 nm).

Remarkably, many features of this picture also hold for doped metallic nanotubes, as shown in Fig. 4. The Fermi level of a pristine metallic tube lies at the center of a subband which contributes a small and constant density of states. Upon doping, this subband forms a relatively inert background over which appears a response very similar to that of a semiconducting tube. One observes band bending and highly concentrated (though not technically localized) states in the would-be gap. The roughening of the local DOS near the Fermi level seen in the figure is partly an artifact of periodicity and k-point sampling, but it also suggests that backscattering may be stronger than in an extrapolation from the limit of vanishing doping [21].

We lastly consider states bound to isolated impurities, using both SCTB and an effective mass approximation. These studies reveal new diameter-dependent scaling relations [22]. A surface charge density $\rho_m = (Q_m/2\pi)\delta(z)e^{im\phi}$ on a cylinder of radius R(ϕ is the azimuthal angle, z, axial position) produces a potential at $(z, \phi = 0)$ which falls off asymptotically ($z \to \infty$) as

$$V_m(z) \sim \frac{(2|m|)!}{2^{3|m|}(|m|!)^2} \frac{Q_m/\tilde{\epsilon}}{\sqrt{z^2 + 2R^2}} \left[\frac{z^2}{2R^2} + 1\right]^{-|m|}. \quad (1)$$
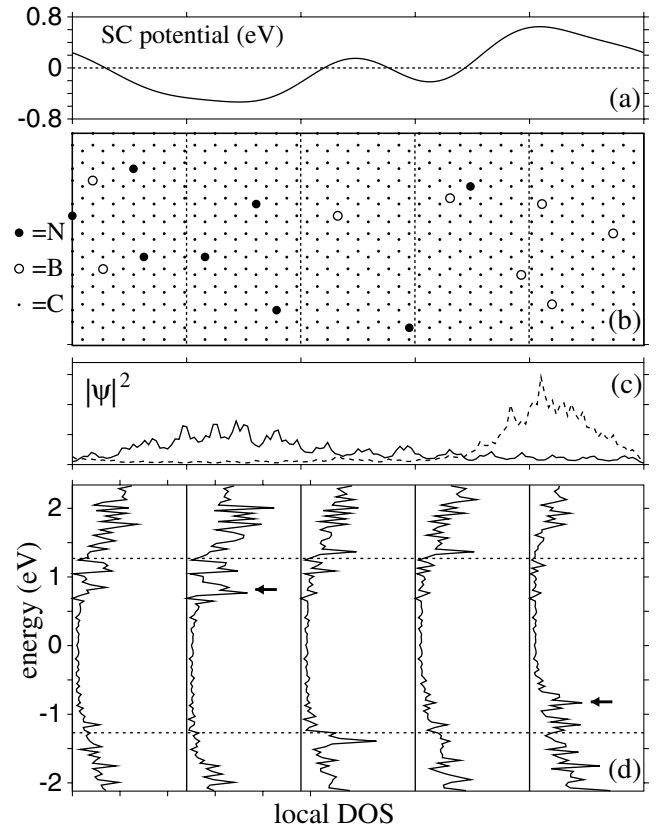
This familiar result of multipole expansion shows that only the $m = 0$ component of charge has an influence of any appreciable range. We retain only the $m = 0$ component of the impurity Coulomb field, partly due to this estimate, but mostly because $m \neq 0$ contributes only if there is band mixing. The $m = 0$ component of the potential can be written explicitly as an integral, but it differs little from the potential of an identical charge located on the tube axis, so we use the latter for simplicity, taking the charge to be $Z|e|$. Ignoring the trigonal distortion of the nanotube electronic structure, the band-slicing picture gives an effective mass $m^* = E_{\text{gap}}/(2v_F^2)$, with which we obtain the one-dimensional wave equation,

$$\frac{d^2\psi}{d\zeta^2} = -\left(\frac{E_{\text{gap}}R}{\hbar v_F}\right)^2 \left[\frac{E}{E_{\text{gap}}} + \frac{Ze^2}{\tilde{\epsilon}RE_{\text{gap}}} \frac{1}{\sqrt{1 + \zeta^2}}\right]\psi, \quad (2)$$

where $\zeta = z/R$ is the axial coordinate scaled by the tube radius. The band gap of a large-gap nanotube (one whose wrapping indices do not differ by a multiple of three) satisfies $E_{\text{gap}}R = 2\hbar v_F/3$. Therefore, if $Z/\tilde{\epsilon}$ is held fixed, both E/E_{gap}, the ratio of bound state energy to the gap, and $\psi(z/R)$ are independent of tube radius. Surprisingly,

the bound state size and energy scale with the diameter of the tube.

The energies and axial spreads of the bound states are determined numerically from Eq. (2). Empirically, both scale extremely well with $Z/\tilde{\epsilon}$ between 1 and 10. We find

$$E/E_{\text{gap}} \approx -2.65(Z/\tilde{\epsilon})^{1.25},$$
$$\langle (z/R)^2 \rangle \approx 1.2(Z/\tilde{\epsilon})^{-1.05}. \tag{3}$$

These results are consistent with self-consistent tight binding. Our SCTB calculation for an $(8,0)$ nanotube with one nitrogen or boron impurity per 7.7 nm unit cell verifies the existence of a bound state fairly well localized within that region ($\langle \Delta z \rangle \simeq 3.2R$). Since the calculation assumes a periodicity, the average potential in the unit cell does not correspond to that of an isolated impurity, so we must subtract the relevant offset. This procedure is somewhat uncertain since $\tilde{\epsilon}(k)$ varies from 7 to 4.5 as kR falls from 1.0 to 0.3. Assuming $k = 2\pi/(\text{cell length})$ gives a binding energy of about $0.23E_{\text{gap}}$. This value is duplicated by Eq. (3) with $\tilde{\epsilon} = 7$, which is reasonable due to the importance of the short-range part of the potential. With $\tilde{\epsilon} = 7$, the model predicts a spread $\langle \Delta z \rangle \simeq 3R$, very close to the SCTB result.

In summary, the pointlike character of dopant charges in B/N substitutionally doped nanotubes is important at all doping levels. At high doping, fluctuations spontaneously produce a high density of nonlinear nanometer-scale quantum dot and/or junction structures, which are relatively insensitive to environmental perturbations such as packing into nanotube bundles (note that these junctions do not simply provide scaled-down traditional functionality). These results are also relevant to chemisorbed dopants. The one-dimensional nature, which makes doping variation especially relevant to electronic characteristics, also facilitates mapping and manipulation, e.g., by scanning tunneling microscopy. Using fluctuations in this way can produce nonlinear device characteristics on scales far smaller than can be fabricated intentionally and avoids the need for fine doping control.

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