Pure Carbon Nanoscale Devices: Nanotube Heterojunctions

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Introduction of pentagon-heptagon pair defects into the hexagonal network of a single carbon nanotube can change the helicity of the tube and alter its electronic structure. Using a tight-binding method to calculate the electronic structure of such systems we show that they behave as nanoscale metal/semiconductor or semiconductor/semiconductor junctions. These junctions could be the building blocks of nanoscale electronic devices made entirely of carbon.

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Helicity has a profound effect on the electronic structure of carbon nanotubes [1,2]. All nonchiral, armchair (n, n) tubes are metals. Excepting those of very small radius [3], all (n, m) tubes with $n - m$ a nonzero multiple of three are small gap semiconductors or semimetals [1]. The remaining tubes are semiconductors with band gaps roughly proportional to the reciprocal of the tube radius [4].

Instead of comparing the electronic structures of tubes with different helicities, we consider changes in helicity *within a single tube.* The chirality of a tube can be changed by introducing topological defects into the hexagonal bond network [5]. The defects must induce zero net curvature to prevent the tube from flaring or closing. Minimal local curvature is desirable to minimize the defect energy. The smallest topological defect with minimal local curvature and zero net curvature is a pentagon-heptagon pair. A pentagon-heptagon defect pair with symmetry axis nonparallel to the tube axis changes the chirality of a nanotube by one unit from (n, m) to $(n \pm 1, m \mp 1)$. Figure 1 shows an (8,0) tube joined to a (7,1) tube. The highlighted atoms comprise the defect. We denote this structure by (8,0)/(7,1), in analogy with interfaces of bulk materials. Within a tight-binding model, far from the interface the (7,1) half tube is a semimetal and the (8,0) half tube is a moderate gap semiconductor. The full system forms a quasi-1D semiconductor/metal junction. Unlike most semiconductor/metal junctions [6], the (8,0)/(7,1) junction is composed of a single element.

We use a tight-binding model with one π orbital per atom along with the surface Green function matching method (SGFM) [7] to calculate the local density of states (LDOS) in different regions of two archetypal $(n_1, m_1)/(n_2, m_2)$ systems. In particular, we examine the (8,0)/(7,1) semiconductor/metal junction and the (8,0)/(5,3) semiconductor/semiconductor junction formed with three heptagon-pentagon pairs. In both cases the unit cells of the perfect tubes match at the interface without the addition of extra atoms.

The unit cells of the perfect (7,1) and (8,0) half tubes may be matched uniquely with a single pentagon-heptagon pair. The interface between the unit cells of the (8,0) and (5,3) half tubes contains three heptagons, three pentagons, and two hexagons. Two different matching orientations are possible: one with the two hexagons adjacent, the other without. We choose to study the configuration in which the hexagons are separated from each other. The sequence of n-fold rings around the circumference is then 6-7-5-6-7-5-7-5.

In the tight-binding π-electron approximation [8], the (8,0) tube has a 1.2 eV gap [1] and the (7,1) tube is a semimetal. Within tight binding, these tubes form an

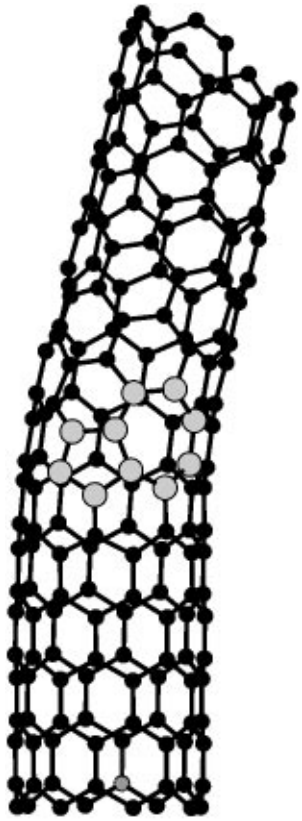

FIG. 1. Atomic structure of an (8,0)/(7,1) tube. The large light-grey balls denote the atoms forming the heptagon-pentagon pair.

archetypal semiconductor/metal junction. We note that curvature-induced σ-π hybridization modifies these band gaps. In particular, within the local density approximation the gap of the (8,0) tube is 0.62 eV [3] and the (7,1) tube is a small-gap semiconductor [4]. For the purposes of examining the generic, qualitative features of carbon nanotube heterojunctions, we restrict ourselves to the π-electron tight-binding treatment in which (8,0)/(7,1) is a semiconductor/metal junction. Within the same picture, the band gap of the perfect (5,3) tube is 1.4 eV [9], 0.2 eV larger than that of the (8,0) tube. The (8,0)/(5,3) junction thus provides a prototypical example of a semiconductor heterojunction.

We examine the local density of states in various regions on both sides of the (8,0)/(7,1) and (8,0)/(5,3) junctions. Our π-electron tight-binding Hamiltonian is of the form

$$H = -V_{pp\pi} \sum_{\langle ij \rangle} a_i^\dagger a_j + \text{ c.c.}, \qquad (1)$$

where i and j are restricted to nearest neighbors, and $V_{pp\pi} = 2.66$ eV [10]. The on-site energy is set equal to zero. Within this theory, graphite sheets and defect-free nanotubes have complete electron-hole symmetry with their Fermi levels at zero. For simplicity all nearest-neighbor hoppings are assumed to be equal, independent of the length, location, and orientation of the bonds on the matched tubes. Deviations in bond lengths due to reconstruction near the interface are neglected. Hence, we study the changes in local electronic structure solely due to changes in the *connectivity* of the lattice.

To determine the LDOS of two joined semi-infinite tubes, we calculate the Green function using the SGFM method. Details about this formalism can be found elsewhere [7]. The SGFM technique allows us to calculate the Green function of a composite system formed by joining two semi-infinite media from the Green functions of the two infinite constituent systems. Thus, knowing the Green functions of the pure (n_1, m_1) and (n_2, m_2) tubes, we can easily construct the Green function of the system formed by joining two semi-infinite tubes, $(n_1, m_1)/(n_2, m_2)$. Knowledge of the Green function allows us to extract the local density of states at any site on the matched structure.

The results for the (8,0)/(7,1) matched tube are plotted in Figs. 2 and 3. Figure 2 shows the unit-cell averaged LDOS for three unit cells of the (8,0) half of the matched tube, and for comparison, the DOS of a perfect (8,0) tube. The unit cells are numbered beginning from the junction, so cell 1 of (8,0) is at the interface, in contact with cell 1 of (7,1). We average the LDOS over each cell because quantum interference effects distort the LDOS on individual atomic sites. The unit cell of the (8,0) tube is a circumferential ring of hexagons containing 32 atoms. As the unit cell of the (7,1) tube has 76 atoms, we choose in Fig. 3 to plot the LDOS on the (7,1) side averaged over 32-atom rings. In this way the local densities of states on either side of the system can be directly compared as a function of distance from the interface.

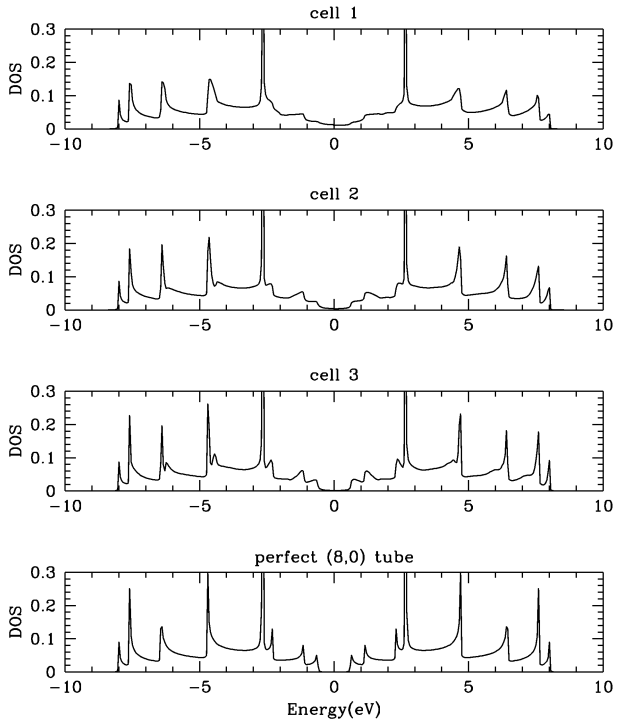

FIG. 2. Results for the (8,0)/(7,1) metal/semiconductor tube. From top to bottom, LDOS at cells 1, 2, and 3 of the (8,0) side, and DOS for a perfect semiconducting (8,0) tube. Cell 1 is at the interface.

In Fig. 2 we see that the LDOS on the (8,0) semiconducting side of the junction is most distorted in cell 1, the region nearest the interface. A coincidental alignment of the bands farthest from the Fermi level in the asymptotic regions on either side of the junction implies that the difference from the perfect-tube DOS is biggest for energies near the gap for this specific junction. In particular, cell 1 shows allowed states in the energy range of the gap of the infinite (8,0) tube. These metal-induced gap states [11] are characteristic of a metal-semiconductor junction. These states swiftly disappear as we move into the semiconductor, as shown in the plots for cells 2 and 3. Moving away from the interface, the perfect-tube DOS features are recovered: in cell 3, all the Van Hove singularities of the infinite tube can be clearly identified.

Unlike the semiconductor side of the system, the LDOS around the Fermi energy (0 eV) in the metallic (7,1) half tube remains largely unchanged. In ring 1, most of the Van Hove singularities present in the perfect (7,1) tube DOS are smeared out, with the exception of those at the highest and lowest energies. As expected, the features of the infinite (7,1) tube are gradually recovered when moving away from the defect region. All the features of the perfect (7,1) system are identifiable in ring 3.

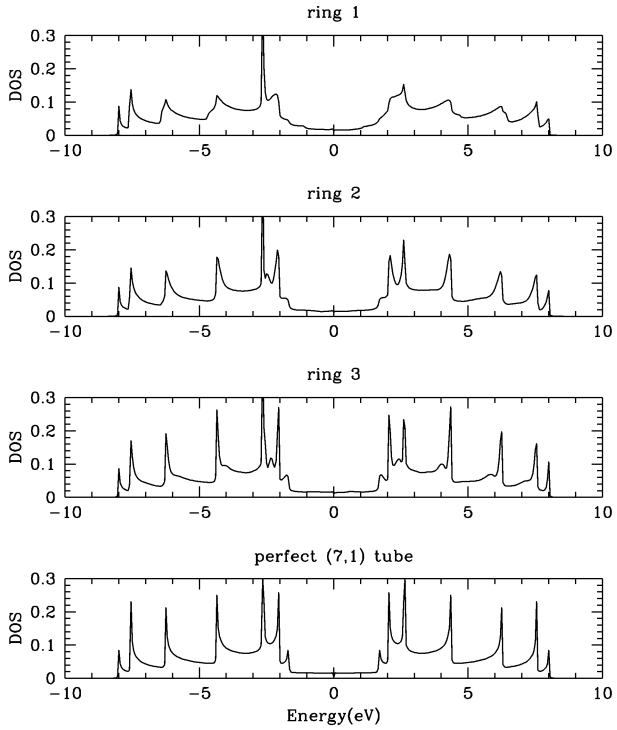

FIG. 3. Results for the (8,0)/(7,1) metal/semiconductor tube. From top to bottom, LDOS at rings 1, 2, and 3 of the (7,1) side, and DOS for a perfect metallic (7,1) tube. Ring 1 is at the interface.

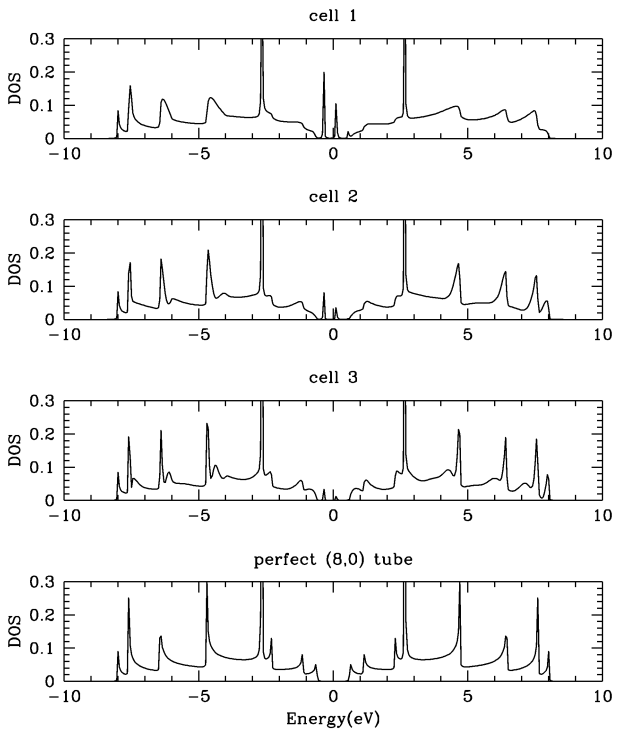

FIG. 4. Results for the (8,0)/(5,3) semiconductor/semiconductor tube. From top to bottom, LDOS at cells 1, 2, and 3 of the (8,0) side, and DOS for a perfect semiconducting (8,0) tube. Cell 1 is at the interface.

The results for (8,0)/(5,3) semiconductor/semiconductor heterojunction are plotted in Figs. 4 and 5. As for the previous case, we plot the LDOS on the (5,3) side averaged over 32-atom closed rings, instead of unit cells. Two defect states appear in the gap near the interface. The geometric distortions due to the three pentagon-heptagon pairs in the matching region create states in the gap in a manner similar to that seen in bulk semiconductor interfaces. As we have not changed the bond distances at the matching region, we attribute the appearance of these states to the changes in the lattice connectivity, that is, to the alteration of the network topology. These interface states may pin the Fermi energy of the system [12].

The interface states have maximal local density of states in cell 1 of the (8,0) tube, the narrow-gap semiconductor of the junction. Their amplitudes are appreciable in five consecutive 32-atom rings, a 12 Å length along the tube axis. The amplitudes decay faster in the (5,3) side of the system. This behavior is to be expected, for (5,3) is the wide-gap semiconductor of the junction. As already seen in the previous system, the LDOS in the interface region is the most distorted; the pure (5,3) and (8,0) features appear when moving far from the defect region. The prominence of the interface states in this junction is a consequence of the presence of three pentagon-heptagon defects. Other, less calculationally convenient junctions with comparable band offsets can be obtained with only a single defect and consequently a much reduced density of interface states.

Chirality-changing pentagon-heptagon defects provide a wide range of device possibilities for doped and undoped carbon nanotubes. By arranging these defects along the length of a carbon nanotube one could modulate the electronic structure and generate a variety of carbon-based quasi-1D quantum wells and superlattices with band offsets of $\sim 0.1\,\mathrm{eV}$. Assuming a suitable third terminal could be introduced adjacent to a semiconducting barrier within a metallic nanotube, one can easily envision a gated conductive channel. The Fermi level of a metallic pure carbon nanotube lies within the gap of a similar semiconducting tube. As such, either *n*-type or *p*-type doping of the semiconducting side of a metal/semiconductor interface should yield a device similar to a Schottky barrier.

The experimental signature of a pentagon-heptagon defect is an abrupt bend between two straight sections of nanotube. We used a tight-binding molecular dynamics scheme [13] on finite systems to determine the bend angles. For a junction with a single pentagon-heptagon pair we obtained angles of roughly $\sim 0-15°$, the exact value depending on the particular tubes involved. We have recently become aware of an experimental observation of a localized $\sim 14°$ bend in a multiwalled pure carbon nanotube [14].

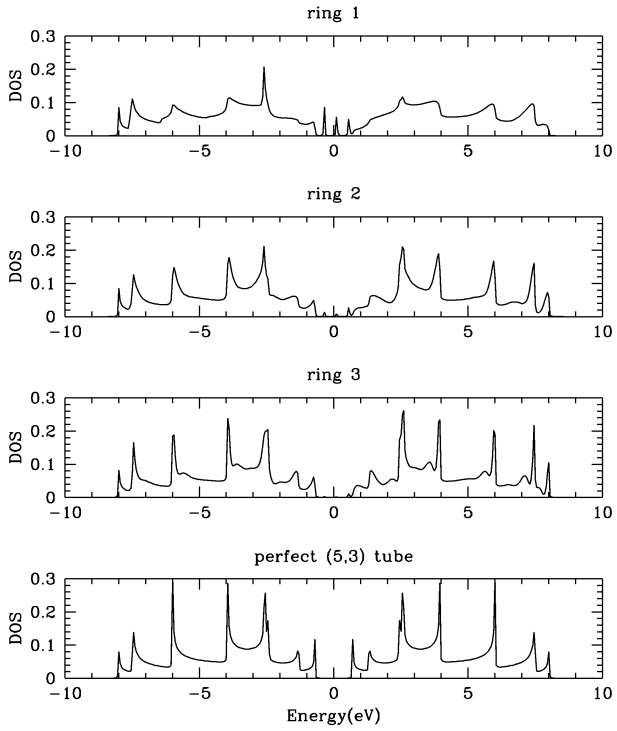

FIG. 5. Results for the (8,0)/(5,3) semiconductor/semiconductor tube. From top to bottom, LDOS at rings 1, 2, and 3 of the (5,3) side, and DOS for a perfect semiconducting (5,3) tube. Ring 1 is at the interface.

In summary, we have proposed a new type of metal/semiconductor or semiconductor/semiconductor junction, made of a single element, and based solely on the introduction of topological defects in the hexagonal graphite network of the carbon tubules. We have calculated the LDOS within the tight-binding approximation for two archetypal systems. If produced, these junctions could be the building blocks of nanoscale semiconductor devices.

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