Quantum Size Effects in Carbon Nanotube Intramolecular Junctions

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ABSTRACT

We calculated the effect of varying the length of a metal-semiconductor carbon nanotube junction on its electrical properties. Joining a metallic (5,5) tube to a semiconducting (10,0) tube leads to the creation of new states near the Fermi energy and produces a larger conductance gap (about 2 eV) than the band gap of the semiconducting segment (about 1 eV). The new states reflect the charge transfer from the (5,5) to the (10,0) segment. The larger conductance gap is due to the mismatch in the conducting states of the (5,5) and (10,0) segments. Although the number of states in the vicinity of \( E_F \) increases significantly with increasing nanotube length, the electrical behavior of the junction does not acquire the characteristics of the semiconducting segment. The calculations suggest that the (5,5)/(10,0) nanotube junction could behave as an intrinsic diode for lengths as small as 4 nm.

The possibility of connecting segments of different types of carbon nanotubes (CNTs) to produce new building blocks for future nanoelectronic devices and circuits has generated intense interest. One could, for example, produce a carbon nanotube junction (CNTJ) from two segments of tubes with different chirality, for example a metallic and a semiconducting tube, to form a single molecule diode. Several types of junction have been experimentally and theoretically considered; an intramolecular junction where tubes with different chirality are connected through pentagon-heptagon pair defects or other types of defects, a crossed-linked junction where tubes are simply stacked in a cross-like fashion without chemical bond formation, and more complex structures such as a Y-junction. There have been experimental confirmations of the rectifying behavior of junctions, however, the observed large suppression of the current was not predicted by tight-binding calculations. Chico has shown in the case of a metal–metal junction that a symmetry difference between two conduction channels leads to a total reflection of ballistic electrons at the CNT–CNT interface. Here we investigate the conductance gap opening for the case of a metal-semiconductor intramolecular junction and explore the effect of electron confinement on the electrical properties of a CNTJ.

The carbon nanotube model used in this study is a (5,5)/(10,0) (metal/semiconductor) junction containing 5- and 7-membered rings at the interface (see left panel in Figure 1). Joining the (5,5) and (10,0) segments lowers the entire symmetry of the system to \( C_{5v} \). The first valence and conduction bands of the armchair (5,5) segment belong to the \( A \) irreducible representation in the \( C_{5v} \) symmetry group, and to the \( E \) representation for the (10,0) segment. The electrical transport properties of this intramolecular carbon nanotube junction were computed using a Green’s function approach within the Landauer–Büttiker formalism. The two tubes are bonded with their dangling bond bearing ends to two gold electrodes. Each electrode is modeled by a layer...
of 22 gold atoms in a (111) crystalline arrangement. The Green’s function $G_{NT}$ of the combined electrode-nanotube-electrode system is written in the form

$$G_{NT} = [ES_{NT} - H_{NT} - \Sigma_1 - \Sigma_2]^{-1} \quad (1)$$

where $S_{NT}$ and $H_{NT}$ are the overlap and the Hamiltonian matrices, respectively, and $\Sigma_{1,2}$ are self-energy terms that describe the effect of the electronic structure of the two leads. The Hamiltonian $H_{NT}$ and overlap matrices are determined using the extended Hückel (EH) model with $s$, $p_y$, $p_z$ orbitals for each carbon atom and one $s$ orbital for each gold atom ($s$ orbitals dominate the density of states of gold near $E_F$). Finally, the transmission function $T(E)$ is given by

$$T(E) = T_{21} = \text{Tr}[(\Gamma_2 G_{NT} \Gamma_1 G_{NT}^{-1})] \quad (2)$$

where $\Gamma_{1,2} = i(\Sigma_{1,2} - \Sigma_{1,2}^\dagger)$.

Figure 1 gives the transmission function (upper-right panel) and the density of states (DOS) diagrams (lower-right panel) of the individual metallic $(5,5)$ (A) and semiconducting $(10,0)$ (B) components that form the metal-semiconductor (C) nanotube junction. The lengths of the tubes are similar, $\approx 100$ Å. The transmission function for the metallic $(5,5)$ tube is similar to that which we obtained for a $(6,6)$ tube. The conductance at $E_F$ of 2.3 $e^2/h$ compared to the ballistic value of $4 e^2/h$ suggests an additional resistance of 5 kΩ originating from the imperfect coupling at the NT–Au contacts. The small decrease in conductance at positive energies is related to the nanotube–electrode geometry. The transmission curve for the $(10,0)$ tube shows very weak conduction at $E_F$ ($T(E_F) < 10^{-6}$), and the conductance gap ($\approx 0.9$ eV) is in agreement with the calculated band gap (see lower-right panel and ref 17). The electrical characteristics of the CNTJ, on the other hand, strongly contrast those of the individual components: the transmission at $E_F$ is more than 4 orders of magnitude lower than for the $(10,0)$ tube, and the conductance gap is almost twice that of the $(10,0)$ tube. In addition, the DOS of the CNTJ contains several new features near $E_F$ that are absent in the individual $(5,5)$ and $(10,0)$ components. Since transport in the $(5,5)$ segment is ballistic, the lower $T(E_F)$ for the CNTJ reflects the backscattering of electrons at the $5–7$ interface. The larger conductance gap of the CNTJ suggests an absence of matching conduction channels between the metallic and the semiconducting nanotube segments.

In Figure 2, we plot the local density of states (LDOS) in the vicinity of the $5–7$ interface of three CNTJs with lengths of 54, 103, and 190 Å (each CNTJ contains $(5,5)$ and $(10,0)$ segments with similar length). Each of these curves represents the contribution from a carbon ring that contains 20 carbon atoms arranged in an armchair $(5,5)$ or zigzag $(10,0)$ structure. Charge transfer from the metallic $(5,5)$ to the semiconducting $(10,0)$ tube leaves the latter tube negatively charged. The upper-left panel of Figure 3 demonstrates this charge transfer. Its dependence on the tube length will be discussed below. The more striking DOS feature is the presence of a sharp peak just below $E_F$ (at around $-0.15$ eV) in carbon rings near the $5–7$ interface. These low energy states at $-0.15$ eV are found in both $(5,5)$ and $(10,0)$ tubes. In the $(5,5)$ tube they are strongly localized on the first two carbon rings, while the $(10,0)$ tube is affected over a longer distance of around 15 Å from the $5–7$ interface. This behavior reflects the different screening characteristics of the two segments. Far from the $5–7$ interface, the electronic properties (especially the band gap) of the individual $(5,5)$ and $(10,0)$ tubes recover their “bulk” values.

From the LDOS diagrams, we can also clearly observe the presence of several sharp features, especially in the $(5,5)$
tube. The energy spacing ($\Delta E$) between them decreases with an increasing CNTJ length. The presence and position of the fine structure is reminiscent of the level splitting produced by quantum size effects that become negligible for long carbon nanotube models such as the 190 Å long model. The dotted lines in Figure 2 indicate the position of states near the Fermi level in the metallic (5,5) tube and their relation with bands in the (10,0) tube. It is clear that both tubes have a few energy bands in common near $E_F$ that would allow electron conduction in a CNTJ with a length less than 100 Å. On the other hand, the (5,5) segment in the long 190 Å model shows a significant number of states near $E_F$ that would energetically match with states in the first conduction (valence) band of the (10,0). In addition to the energy matching, one has also to take into account rotational symmetry considerations.4

Although the low-lying energy states near $E_F$ could scatter electrons, their presence cannot easily explain the large conductance gap observed in Figure 1 for the (5,5)/(10,0) junction. Quantum size effects on the transport in CNTJ are seen in the main panel of Figure 3 where a strong dependence of the transmission function on the length of the tube, which varies from 22 to 190 Å, is observed. The dotted lines represent the raw transmission function, while full lines are smoothed curves. The conductance at $E_F$ decreases exponentially with an increasing length as expected from the presence of the semiconducting (10,0) tube, but the conductance gap remains constant ($\approx 2$ eV) over the entire range of length investigated. Another interesting feature in these curves is the presence of fine structure perceptible through the several resonances seen in the conductance curves. We report, in the upper-right panel, the spacing between these conductance resonances as a function of CNTJ length. The spacing is directly proportional to the inverse of the length ($1/L$) such as discrete molecular orbitals are gradually transformed into bands in agreement with the quantum size effect observed with metallic carbon nanotubes.18,19 Electrons originating from the (5,5) tube have an increasing probability to cross the 5–7 interface to the (10,0) tube through the interface states (or resonance states). However, since these disappear far from the interface in the (10,0) tube, the electrons are scattered and the overall conductance remains low. The nonzero conductance at $E_F$ found for the very short (<30 Å) junction can be understood by noting that the interface states centered around $-0.15$ eV are present along the entire (10,0) segment and constitute a possible conduction channel. Furthermore, the conduction into these very small devices could also be partly explained through metallization induced by the gold contacts and by electron tunneling. For longer CNTJs, even though the number of states around $E_F$ increases with the length, the conductance at $E_F$ continues to decrease rapidly. The 190 Å long CNTJ studied is quite interesting since there is an energy matching between conduction states that produces a sharp increase (about 6 orders of magnitude) in the transmission function around 0.5 eV (see Figure 3), which, however, is unable to produce an effective electrical transport; most of the electrons are reflected at the 5–7 interface. The calculated asymmetry of the transmission curves due to the enlarged conductance band gap agrees well with previous experimental observations of a strong current suppression in the rectification behavior of a metal-semiconductor junction.8

The variation of charge transfer with the CNTJ length reported in the upper-left panel of Figure 3 is also directly related to quantum size effects. These two curves correspond to the accumulation of charges20 within the first four carbon rings in each (5,5) and (10,0) tube away from the 5–7 interface. Short metallic carbon nanotubes are well known to open a band gap and to have a smaller DOS at $E_F$ for $L \leq 50$ Å.18 The increased depletion of electrons from the (5,5) tube with increasing length of CNTJs is essentially due to the increasing DOS at $E_F$. On the other hand, the increasing net charge in the (10,0) tube does not follow the exact opposite trend as the depletion of the (5,5) tube. This difference can be explained with the help of the LDOS diagram shown in Figure 2. The (5,5) segment is perturbed only within a few carbon rings, while the induced states as well as the net charge in the (10,0) tube are extended and redistributed over a larger distance away from the 5–7 interface. The charge-transfer process creates a potential barrier, in addition to that produced by the 5–7 structural defects, and should significantly affect the transport properties of the junction. To determine the potential accurately across the CNTJ, the amount of charge transfer from the (5,5) to the (10,0) tube needs to be quantitatively determined. This would require the use of a self-consistent method in conjunction with an improved Hamiltonian that takes electron–electron interaction into account. This will, however, mostly amplify the effects we described here using the EH approach.

In conclusion, we have shown that joining a metallic and a semiconducting CNT to form an intramolecular junction leads to a charge transfer from the metallic tube to the semiconducting tube and creates new states near the Fermi energy. The number of these resonances increases as a function of the length of the CNTJ, producing an increasing number of states in which electrons can propagate. However, although resonant states are present, most of the electrons are reflected at the 5–7 junction and the overall conductance remains very low over a wide range of energies. The general behavior observed should be valid for other metal-semiconductor junctions. The details would depend on the specific nature of the constituent nanotubes. Finally, the results indicate that the (5,5)/(10,0) nanotube junction has the rectification characteristics of a diode for lengths as small as 4 nm.

References

(20) The net charge was evaluated from a Mulliken analysis of the extended Hückel (EH) calculations. We are not pretending to determine a quantitative charge distribution within EH theory, even if the present description of a charge transfer is qualitatively correct.