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Madhu Menon

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University of Kentucky
University of Kentucky Research Foundation
109 Kinkead Hall
Lexington, KY 40506 -0057

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14. ABSTRACT
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All the structures investigated were fully relaxed using quantum tight-binding molecular dynamics methods and

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Nanoelectronics of Carbon Nanotube Multi-terminal Junctions: (Final Report for W911NF0510372)

Madhu Menon
Center for Computational Sciences
University of Kentucky
Lexington, KY 40506-0045
Phone: (859) 257 8737
Fax: (859) 323 1029
E-mail: madhu@ccs.uky.edu

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Abstract

Using the support we have developed and used a novel method to investigate molecular electronic device applications of carbon nanotube multi-terminal junctions in the form of T- and Y-junctions. The theoretical methods included (i) large scale simulations using accurate quantum tight-binding molecular dynamics scheme and (ii) quantum conductivity formalisms. Both methods were developed by the PI's group. All the structures investigated were fully relaxed using quantum tight-binding molecular dynamics methods and their current vs voltage (I-V) characteristics determined.

1 Introduction

Nanoelectronics of low dimensional materials provide an interesting study from a fundamental physics of the bonding at microscopic level. These materials also have useful potential in technological applications. As semiconductor device development advances towards smaller devices and larger integration density, the effort required for producing each new generation of memory and logic structures increases. Molecularly perfect single-wall carbon nanotubes (SWCN) are the kind of material possessing unique structural and electrical properties that are expected to execute a "quantum" leap in the area of nanoscale electronics.

The most difficult task standing in the way of the use of SWCN in nanoelectric applications is the realistic characterization of the details of contact to the outside terminals for the study of conductance. The details of metal/nanotube hetero-junctions need to be incorporated in the overall circuit design.

Theoretical calculations can provide a very valuable guidance in this area. With accurate determination of the microscopic structures of these molecular devices as a first step,

these calculations can subsequently be used to determine the detailed electronic properties of these devices in a manner useful to experimentalists. Any realistic theoretical determination of structural properties of materials of technological interest must involve the use of molecular dynamics methods. Molecular dynamics simulations can be used as an "experimental" technique to accurately describe a specific material or process. Furthermore, since the goal is to gain a fundamental understanding of structural and electronic properties at the nanoscale regime, the molecular dynamics calculations have to be based on quantum mechanics.

Currently, no such simulations have been undertaken. This is due to the difficulty in accurately characterizing metal-carbon nanotube interactions.

Using the ARO support we have used quantum generalized tight-binding molecular dynamics (GTBMD) method, developed by the PI, to study nanoelectronic properties of carbon nanotubes. The theoretical methods included (i) large scale simulations using accurate quantum tight-binding molecular dynamics scheme and (ii) quantum conductivity formalisms.

2 Theoretical Methods

2.1 Generalized tight-binding molecular dynamics method

The theoretical simulations were performed using a generalized tight-binding molecular-dynamics (GTBMD) scheme developed by the PI Menon that contains many state-of-the-art features[1, 2]. Using this formalism we have performed detailed investigations of various transition metal atoms interacting with single wall carbon nanotubes (SWCN) and find that the curvature of the nanotube and the d-band filling of the d-bands of the transition metal atom has a profound influence on the bonding properties[3]. Using our formalism we have shown the anomalous behavior of conductivity observed in experiment of SWCN to be due to the effects of residual transition metal catalysts residing in close contact with the nanotube walls[4]. Also, we have dynamically simulated, for the first time, the action of Ni in the carbon nanotube growth process[5].

2.2 Quantum Conductivity

Although quantum conductivity calculations of SWCN have been performed by a number of groups, use of several simplifying assumptions in the formalism may severely limit their accuracies while predicting useful device properties. A most common practice is to restrict the tight-binding Hamiltonian to only one π-electron orbital per atom. Furthermore, most of these calculations neglect the effects of structural relaxation altogether. Even while performing relaxation, most use classical many body potentials. Use of tight-binding Hamiltonian for relaxation is very rare.

We have recently developed two formalisms for calculating the quantum conductance of systems consisting of semiconductor and transition metal systems[6, 7]. They are based on the tight-binding description of the system. An attractive feature of both formalisms are that the tight-binding Hamiltonian used in the conductivity calculations is the *same* as that used in structural relaxation. This ensures consistency in our calculations of physical properties.

3 Results

We have investigated the structural and conducting properties of single wall carbon nanotubes (SWCNs) in embedded as well as in side contact with metal leads is obtained using efficient formalisms based on spin polarized tight-binding formulation incorporating full consideration of s, p and d basis sets for carbon and metal atoms. The full structural relaxation of the combined SWCN and metal system is found to be essential for realistic characterization of conductivity. Metal contacting the nanotube and forming metal layer-SWCN-metal layer (ML-SWCN-ML) system consists of several layers, ideally infinite. A few of the metal layers are included as part of the "extended molecule". These consist of: (i) Metal layers in direct contact with the nanotube and, (ii) a few layers that are neighboring to the SWCN. The "extended molecule" consists of nanotube and these two sets of metal layers. The remaining metal layers form the two metal leads (MLs) each of which is semi-infinite. In the present applications, the extended molecule consist of 800-1100 atoms. The entire extended molecule is allowed to fully relax through MD simulations with no symmetry constraints.

The MLs are assumed to be of bulk Ni metal in the $< 001 >$ orientation relative to the nanotube axis (taken to be the z-axis) in the embedded-end contact configuration, while in the side-contact configuration the Ni$< 001 >$ direction is perpendicular to tube axis.

In the embedded end-contact configuration, the open ends of the SWCN are buried into the ML-surface in a way that ML-atoms may bond from both the exterior as well as the interior part of the tube ends. The relaxation results in the distortions of atomic positions for both Ni and C atoms in the contact region. To better illustrate this, Ni atoms from the top panel in Fig. 1 have been removed to obtain the nanotube in the middle panel that shows the distortions of C atoms at the ends. The bottom panel shows distortion free nanotube for comparison.

The calculated I-V curves for three embedded-contact configurations along with the Ni removed SWCN system (Fig. 1, middle panel) are shown in Fig. 2. These were obtained by assuming symmetric biasing i.e., V_L=-V_R=V. The corresponding transmission functions, $T_{\sigma=up}(E)$, are plotted in the inset. From this it can be seen that, for (10,0) SWCN embedded in MLs, noticeable changes are induced in $T_{\sigma=up}(E)$ in going from 3 to 5 metal layers. The changes refer to the location, the width and the strength of the resonance peaks of $T_{\sigma=up}(E)$; they are especially pronounced for energies below the Fermi energy E_F (set to zero), where the $T_{\sigma=up}(E)$ for the system with the 3 metal layers appears larger than that of the 5 metal layers and exhibits a transmission gap at higher energies when compared to those found in the case of the 5 metal layer contact. By further increasing the thickness of the metal layers which is incorporated in the extended molecule, i.e., in going from 5 metal layers to 7 metal layers, it can be seen from Fig. 2 that the differences in the transmission features of the 5 and the 7 metal layer systems are not significant, indicating that convergence has been attained in $T_{\sigma=up}(E)$ with respect to the contact width.

We find that convergence with respect to the number of the metal lead (ML) atoms in contact with the SWCN is found to be very critical. Our results indicate that, in order to maximize device efficiency, one needs to use ML-SWCN systems with a minimal ML-SWCN contact-width to SWCN-length ratio. If this ratio is large enough, the SWCN cannot be seen independently of its contacts and the ML-SWCN-ML system behaves as a molecular wire. Additionally, the ML-SWCN-ML complex is found to have spin-selective transport properties for certain bias range, making it a promising candidate for use as a spin valve in nanoelectronic devices.

We have performed detailed quantum conductivity calculations for complex multi-terminal

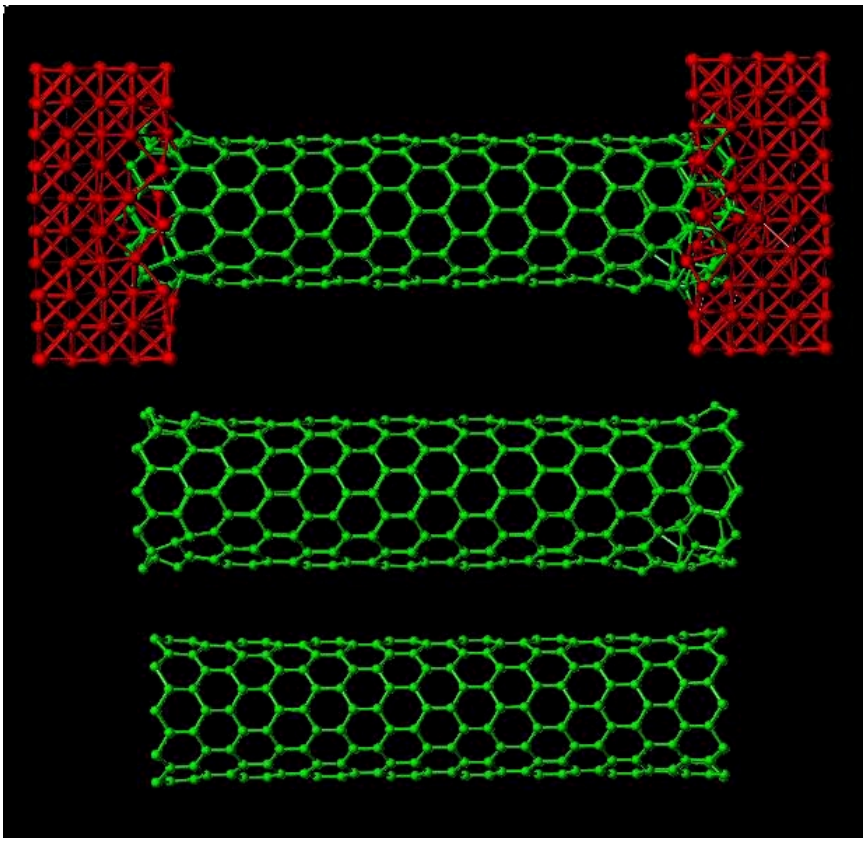

Figure 1: (Color online) Fully relaxed geometry of a (10,0) SWCN in embedded end-contact configuration in Ni (top panel) used in I-V calculations. The middle panel is obtained from removing all Ni atoms from the top panel. The bottom panel shows a fully relaxed isolated (10,0) SWCN.

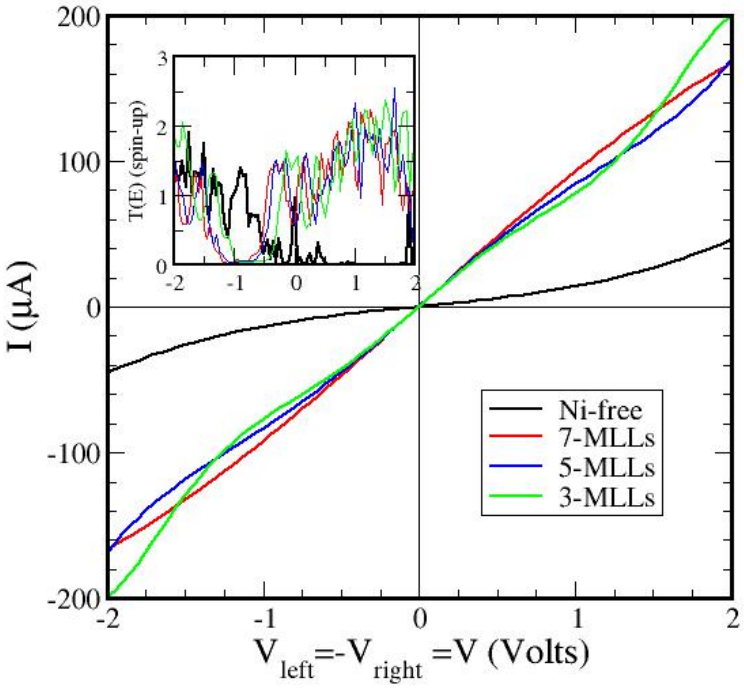

Figure 2: (Color online) Transmission functions for spin-up electrons (upper inset) in units of (e^2/h) and I-V characteristics (current in μA) for symmetric bias configurations for a (10,0) SWCN in three embedded end-contact configurations: (1) In Ni-leads consisting of 7 (red), 5 (blue) and 3 (green) Ni layers. For comparison, the corresponding results for the same nanotube after removing all Ni atoms (Fig. 1, middle panel) are also shown (black curve). The corresponding transmission coefficients are shown by the solid curves in the inset.

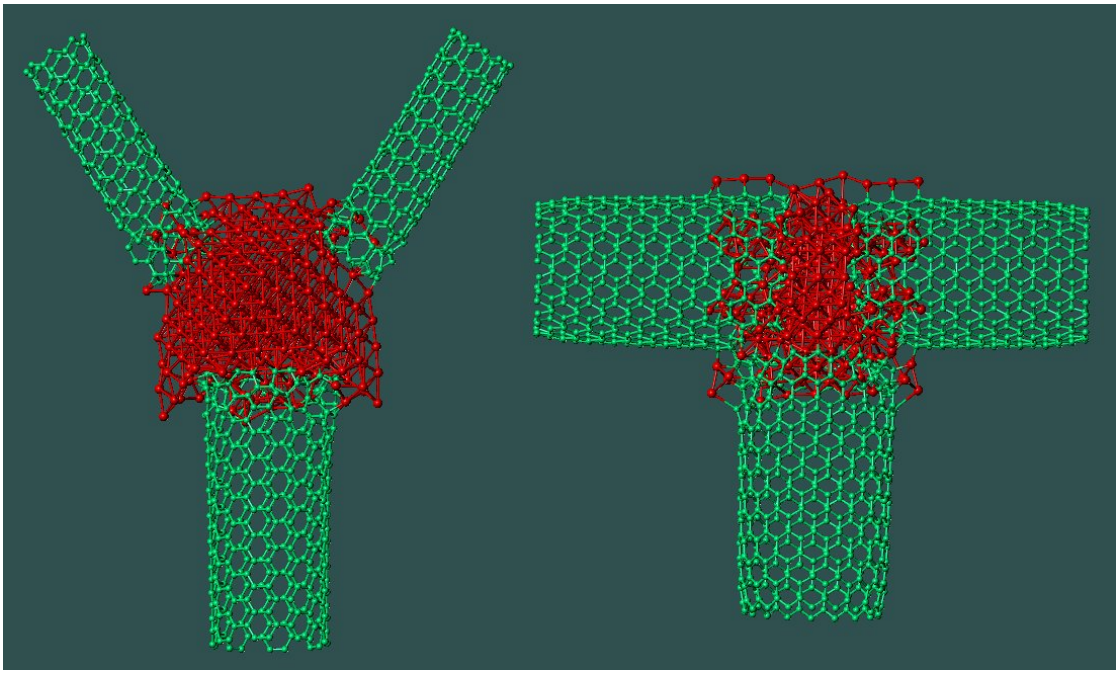

Figure 3: Fully relaxed geometries of two soldered multi-branched junctions made of three SWCN-pieces soldered in the middle by a Ni cluster. The soldering in the right leads to a (10,10)-(18,0)-(10,10) SWCN T-junction while the soldering in the left leads to an (8,0)-(8,8)-(8,0) SWCN Y-junction.

SWCN junctions created by nano-"soldering" with transition metal atoms. In particular, the three-terminal junctions are useful in that they can be used in device applications in which the 3rd terminal can be used for controlling the switching mechanism, power gain, or other transisting applications that are needed in any extended molecular electronic circuit.

In Fig. 3 we show fully relaxed geometries of a (8,0)-(8,8)-(8,0) SWCN Y-junction and a (10,10)-(18,0)-(10,10) SWCN T-junction created by soldering three SWCN branches by Ni clusters. All outer ends of each of the three arms of the T- and Y-junctions are taken to be in contact with the transition metal leads consisting of Ni atoms (not shown).

The I-V curves obtained for the Y-junction in Fig. 3 is shown in Fig. 4. The current directions and the voltages on the three arms are indicated in in the upper inset. The main graph shows the calculated currents in the three arms of the *soldered* Y-junction as a function of the bias voltage V_3. The voltage configuration for this plot has been set to V_1=V_2=0.0 V. This setup makes the Y-junction a two terminal device for the investigation of rectifying behavior. As seen in the figure, there is a noticible increase in the current for positive values of the bias voltage V_3, while for negative values of V_3 the current is negligible. The I-V characteristics, thus, display a distinct asymmetry and rectifying behavior. While this behavior is similar to the *non-soldered* case, although with significantly lower values of the current (lower inset), a striking difference can be observed. The rectification direction for the soldered Y-junction appears to undergo a reversal about V_3=0.

While our results indicate that soldering of multi-branched SWCNs in the form of T- or Y-SWCNs fails to reproduce the transport properties of the corresponding unsoldered junctions

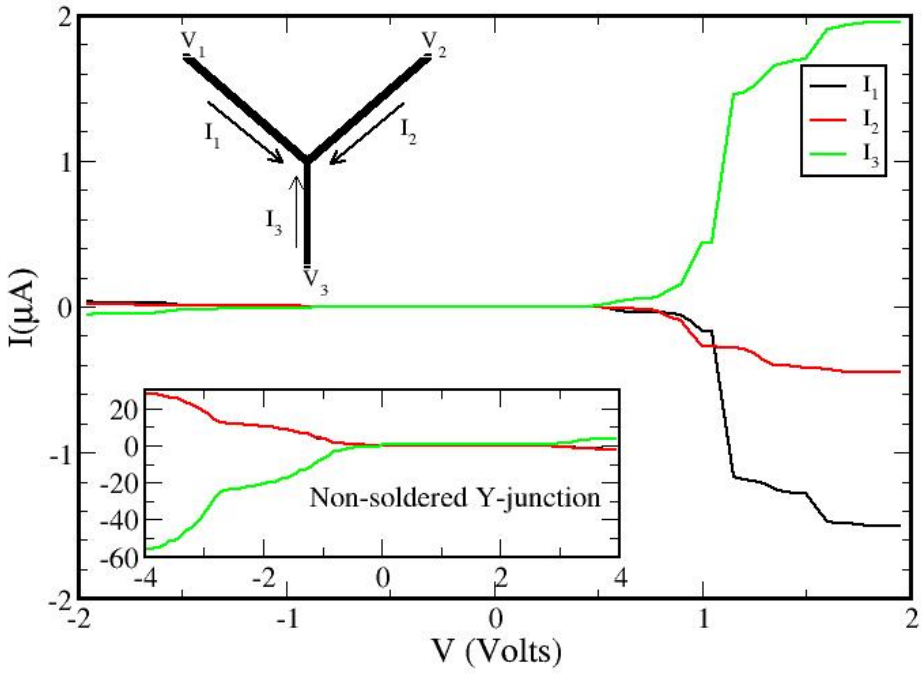

Figure 4: The I-V curves obtained for the soldered Y-junction in Fig. 3 (left). The current directions and the voltages on the three arms are indicated in in the upper inset. The main graph shows the calculated currents in the three arms of the *soldered* Y-junction as a function of the bias voltage V_3. The voltage configuration for this plot has been set to V_1=V_2=0.0 V. The I-V characteristics show asymmetry and rectification. The corresponding I-V curves for the non-soldered Y-junction is shown in the lower inset.

in general, they, however, confirm another important feature: Namely, they demonstrate that the rectifying and switching properties of the Y- and T-junctions are neither the result only of the bias configuration nor the characteristics of the contacts between the tubes and the metallic leads. Because if they were so, soldering could not have such a dramatic effect on the rectification properties. The present results demonstrate that the transport properties of the Y- and T-junctions are strongly depended on their inherent properties as previously demonstrated in our earlier works for the unsoldered junctions.

This inherent characteristic depends on the symmetry of the *"spacer"* region (i.e., the region that joins the three branches) and the way this is bonded to the branches. In the absense of this inherent characteristic, the spacer of the soldered junctions reduces the transport pathways which deviate from the straight trajectories.

Our results have demonstrated that soldering reduces the current as well as the Ohmic character. More importantly, for multi-terminal SWCN junctions, soldering can significantly alter the rectification properties, even reversing its direction due to the destruction of the symmetry of the junction's *spacer* region.

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