

# Electron Transport across Interfaces in Horizontal Carbon Nanofiber Interconnects

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**Abstract**— In a carbon nanofiber (CNF) metal contact such as a bridge between two metallic electrodes, passing high current (current stressing) reduces the total resistance of the system (CNF resistance  $R_{\text{CNF}}$  and contact resistance  $R_c$ ) by orders of magnitude. The role of current stressing is modeled as a reduction in the interfacial tunneling gap with transport characteristics attributed to tunneling between Au and CNF. The model predicts a reduction in  $R_c$  and the nonlinearity in the current-voltage ( $I$ - $V$ ) characteristics gradually disappears as  $R_c$  decreases. These results are consistent with  $I$ - $V$  behavior measured experimentally.

## Introduction

Carbon structures such as carbon nanofibers (CNFs) are expected to play an important role in future electronics, especially in interconnects [1-5]. CNFs belong to the covalent graphene family and have multi-wall stacked-cones with diameters  $d$  ranging from 100 to 200 nm. A four-probe measurement revealed almost linear current-voltage ( $I$ - $V$ ) characteristics, hence CNFs are believed to be metallic [6]. It is pointed out that because of their large  $d$ , it would be difficult to expect quantum confinement effects in CNFs and a resulting semi-conducting phase with a finite bandgap at room temperature [7]. In interconnect applications, CNFs bridge metallic electrodes. So far, structures where CNFs are simply placed on top of pre-fabricated electrodes have been studied. The initial resistance is typically in the  $M\Omega$  range, and current stressing ( $10^5$ – $10^6$  A/cm<sup>2</sup> per fiber) can reduce resistance by two to three orders of magnitude before breakdown occurs as a result of Joule heating [8-10]. In future interconnect applications, CNFs will be contacted to electrodes in a much more repeatable and reliable way, but creating chemical bonds between the CNF and electrodes to form a monolithic electrode-wire structure would be highly challenging. So long as we pursue contacts without involving chemical bonds formation, the drop-cast CNF bridging systems [11] can represent non-monolithic CNF interconnect systems in general. Here, we study such drop-cast CNF bridging systems using a tunneling transport model and show that improvement with current stressing is mainly due to change in the electrode - CNF contact.

## Experiment

In order to study the effect of current stressing, the CNF-electrode system was prepared using Al and W electrodes as in the SEM image in Fig. 1(a) [11], where the CNF was suspended between the electrodes such that the substrate's role in heat dissipation is removed. A battery was used to supply current with a variable resistor  $R_v$  as in the inset of Fig. 1(b).  $R_v$  ranged from two to five times of the summation of the CNF bulk resistance  $R_{\text{CNF}}$  and Au-CNF contact resistance  $R_c$ . The current was increased from zero and the voltage between two electrodes was measured as in Fig. 1(b). As the current was turned on, operating point (OP) moved to A tracing an initial  $(R_{\text{CNF}} + R_c)^{-1}$  line I. Then, OP suddenly moved to B. As the current was further increased, OP moved to C tracing a steeper  $(R_{\text{CNF}} + R_c)^{-1}$  line II. Then, OP moved from D to E tracing a further steeper  $(R_{\text{CNF}} + R_c)^{-1}$  line III. Beyond E, the CNF breakdown occurred due to excess Joule heating.  $R_{\text{CNF}} + R_c$  was 103 k $\Omega$  for line I, and was 3 k $\Omega$  for line III.

Four-probe measurements have shown that the resistivity for unstressed CNF is  $4 \times 10^{-5}$   $\Omega\text{m}$ , consistent with a reported value of  $4.2 \times 10^{-5}$   $\Omega\text{m}$  [6]. For a CNF with  $d \sim 200$  nm and length  $L \sim 4$   $\Omega\text{m}$ , the CNF resistance  $R_{\text{CNF}}$  is estimated to be 5 k $\Omega$ , significantly lower than the measured  $R_{\text{tot}}$  [12], except for the very final stage before breakdown. Thus, the sudden decreases in  $R_{\text{tot}}$  can be attributed to the contact resistance  $R_c$ , which must be associated with physical change at the contacts.

The follow-up experiment uses a CNF grown in a plasma-enhanced chemical vapor deposition process with Ni catalyst [11]. The structure consists of a SiO<sub>2</sub> substrate with Au electrodes as shown in the scanning electron microscope (SEM) image in Fig. 2(a). A CNF is bridged between pre-fabricated Au electrode pairs by drop-cast of CNF in isopropyl alcohol solution [11]. Recent work using this configuration confirmed that  $R_c \gg R_{\text{CNF}}$  except for the final stress cycle before breakdown [10], which is again consistent with the results of the experiment described above. Figure 2(b) shows the typical  $I$ - $V$  characteristics for one fabricated test structure before and after two current stressing cycles with 100  $\mu\text{A}$  and 450  $\mu\text{A}$ , respectively (solid circles are modeling results). In Fig. 2(c), the same data are re-plotted on a logarithmic scale. Over the voltage range tested, current is two to three orders of magnitude higher after two stressing cycles. All other measured samples show a similar response to stressing. To examine this behavior further, we define an  $I$ - $V$  nonlinearity factor,  $\gamma(V) = 0.5 \times I(V)/I(V/2) - 1$  [13]. In the measurement results,  $\gamma$  decreases as  $R_{\text{tot}} = R_c + R_{\text{CNF}} \sim R_c$  decreases, such that  $\gamma(+1V) = 1.0$  (initial), 0.34 (first stressing), and 0.15 (second stressing), respectively. The reduction in  $I$ - $V$  nonlinearity with decreasing  $R_c$  is characteristic of tunneling transport [14-16]. We propose

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that an Au-CNF interfacial region or gap  $z$  exists at the contact and its reduction must be the main mechanism for the reduction in  $R_c$ .

### Tunneling Model

To analyze tunneling transport between Au and CNF, a traditional model for two *identical* metals [14, 16] is extended for two *different* metals. Au has a work function  $q\phi_{\text{Au}}$  of 5.1 eV and a Fermi level  $E_{\text{FAu}}$  of 5.5 eV, while CNF has a work function  $q\phi_{\text{CNF}}$  of 4.6 eV and a Fermi level  $E_{\text{FCNF}}$  of 3.0 eV, estimated with tight-binding theory [17], as shown in Fig. 3. The tunneling barrier with width  $z$  is formed by an interfacial region with possible impurities. In tunneling, the electron total energy  $E$  (measured from the bottom of the Au conduction band), and the electron transverse momentum  $k_{\parallel}$  are conserved at perfect interfaces [18], which is assumed here. The tunneling current is then calculated by considering all contributions satisfying these conservation relations under the bias condition in the context of two *different* metals. The detailed formalism is presented in the Appendix.

When *two* Au-CNF tunneling junctions 1 and 2 with  $z_i$  and  $S_i$  ( $i = 1, 2$ ) are connected in series as in Fig. 2(a), the junction with larger  $z_i$  will determine the total  $I$ - $V$  characteristics. In the present CNF drop-cast method, the initial difference in  $z_i$  and  $S_i$  between two junctions is unavoidable – the difference of 10–20 % is quite common for  $S$  as seen in SEM images, and thus similar difference would be quite possible for  $z$ . Since the current depends exponentially on  $z$ , the junction with the larger  $z$  has much larger tunneling resistance than the other, resulting in one junction dominating the total  $I$ - $V$  characteristics. This is also the case for carbon nanotube tunneling junctions or Schottky junctions [19].

We now apply the single-junction model to the circuit in Fig. 2(a). The current  $I$  is calculated at 300 K using  $I = JS$ , where  $S = 0.125 \mu\text{m}^2$  as before.  $z$  is the only adjustable parameter. The initial experimental  $I$ - $V$  curve has clear asymmetry (if two junctions were identical, the  $I$ - $V$  curve would be symmetric and the single-junction model can no longer apply). Modeling results (circles) for  $z = 8.3, 5.9, \text{ and } 5.0 \text{ \AA}$  of the dominant junction are compared with the measured  $I$ - $V$  at three different current stressing stages in Figs. 2(b) and 2(c). Asymmetry is small in both modeling and measured cases, except for the initial measured  $I$ - $V$ . Charged and/or polarized impurities in the interfacial region could be responsible, but the mechanism has not been identified at this stage. The pre-stressed  $I$ - $V$  is fitted with  $z = 8.3 \text{ \AA}$  and calculated  $\gamma = 0.13$ . The  $I$ - $V$  after the first and second current stressing cycles corresponds to  $z = 5.9 \text{ \AA}$  and  $5.0 \text{ \AA}$ , respectively, with calculated  $\gamma = 0.07$  and  $0.06$ . The trend in calculated  $\gamma$  with decreasing  $z$  is similar to that of the corresponding measured  $\gamma = 1.0, 0.34, \text{ and } 0.15$ , albeit somewhat smaller.

$\gamma$  (as well as  $I$ ) strongly depends on work functions, and they are sensitively dependent on sample preparation, including the choice of catalyst. Here, we have used ideal Au and CNF work functions assuming perfectly clean interfaces. Positively charged surface impurities will make the function shallower, and vice versa [20]. Even when the impurities are neu-

tral, if they are polarized and oriented in a certain direction, it can also influence the work function [21]. Additionally, the image charge effect [14, 16], which effectively modifies the work functions, might be relevant. Such electrostatics in the interfacial region is responsible for the larger  $\gamma$  values observed in the experiment.

According to our model, current stressing reduces  $z$  of the dominant junction. Generally, van der Waals type interactions are common for neutral materials including graphitic structures, and are attractive at longer distances and repulsive at short distances. The crossover distance is the equilibrium distance. These interactions allow CNFs to remain in place, but are also responsible for attracting impurities into the system, adsorbed onto the graphitic sidewalls and electrode surfaces, which forms the interfacial region. Thus, the initial  $z$  tends to be larger than the equilibrium value. As the current increases, Joule heat is generated at the Au-CNF interface and residues will disappear through evaporation, oxidation, or chemisorption, leading to smaller  $z$ . The final  $z$  value of  $5.0 \text{ \AA}$  is close to the equilibrium one but may still be larger, reflecting possible atomic-scale surface roughness. Once this  $z$  is reached, eventually the force will be at the edge of transition to repulsion and no further reduction is expected. This is consistent with our observation that improvement by current stressing does not continue indefinitely. In addition, from SEM images, we have observed local Au deformations at the CNF-electrode interface. This observation suggests changes in interface morphology due to constant current stressing and an effective reduction in  $z$ .

Plombon *et al.* reported high-frequency electrical measurements for a bundle of 10–100 single-wall carbon nanotubes bridging two metallic electrodes [4]. Their nanotube bundle and our single CNF have similar  $d$  and  $L$ . They proposed an equivalent circuit with a contact capacitance  $C_c \sim 7.3 \text{ fF}$  and  $R_c \sim 17 \text{ k}\Omega$  at the electrode-nanotube interface. Using our modeling results of  $z = 5.0 \text{ \AA}$  and assuming a permittivity  $\epsilon$  larger than the vacuum permittivity  $\epsilon_0$  by a factor of 1–10 accounting for impurities, we can estimate  $C_c = \epsilon S/z = (1.8\text{--}18) \text{ fF}$  and  $R_c \sim 12 \text{ k}\Omega$  for our system, which are comparable to the reported value.

### Conclusion

The present findings generally apply to CNF interconnect systems without chemical bond formation between CNF and electrodes. In practical applications, contacts will be created in a much more reliable way, and while CNF bulk quality will also improve. Thus,  $R_c$  might still dominate the total system resistance. Since tunneling transport determines  $R_c$ , it will be possible to improve total system performance by making a more intimate contact (reduce the barrier width) or by placing charged and/or polarized impurities intentionally in the interfacial region so that the CNF and electrode work functions are decreased (reduce the barrier height).

In summary, electron transport properties of a CNF bridging electrodes are studied and compared to tunneling single-junction model results. The model explains the key features of the measured  $I$ - $V$  data, including improvement in  $I$ - $V$  linearity

with decreasing  $R_c$ . The effect of current stressing is to reduce the interfacial gap, possibly through change in interface morphology and impurity reduction as a result of Joule heating.

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### Appendix: CNF-Au Tunneling Model

The energy band structure of a CNF-Au contact is plotted in Fig. 3. CNF is biased at  $V$  with respect to grounded Au, and thus, the Fermi levels are related by

$$E_{FAu} - qV = E_{FCNF}, \quad (1)$$

where  $-q$  is the electron charge. The tunneling barrier of a width  $z$  is formed by an interfacial region with possible impurities. In tunneling, there will be no force in the transverse directions at perfect interfaces and the electron transverse momentum  $k_{\parallel}$  is conserved. Thus, we have,

$$k_{\parallel Au} = k_{\parallel CNF} \equiv k_{\parallel}. \quad (2)$$

The electron total energy  $E$  is also conserved (measured from the bottom of the Au conduction band). Thus,

$$\frac{\hbar^2}{2m_{Au}}(k_{\parallel}^2 + k_{\perp Au}^2) = E_{CNF}(k_{\parallel}, k_{\perp CNF}) + \Delta E_c \equiv E. \quad (3)$$

Here,  $k_{\parallel}$  ( $k_{\perp}$ ) is a parallel (perpendicular) momentum,  $\hbar$  is a Planck constant, and  $m_{Au}$  is the electron mass in Au.  $E_{CNF}$  is the dispersion in CNF.  $\Delta E_c$  is the conduction band bottom difference between Au and CNF, equal to 2.5 eV. This means that if an electron tunnels from region  $l$  to region  $m$  ( $l, m = \text{Au}$  or CNF), it loses or gains kinetic energy due to the finite  $\Delta E_c$  even in thermal equilibrium. Since the tunneling current depends on the electron longitudinal velocity  $v_{\perp}$ , we need to take that into account in the present CNF-Au (two different metals) tunneling problem.

The tunneling current density  $J_{m \leftarrow l}$  from region  $l$  to region  $m$  is given by

$$J_{m \leftarrow l} = -q \sum_{\vec{k}, spin} n(\vec{k}) v_{\perp}(k_{\perp}) (1 - f_m) T_t f_l, \quad (4)$$

where  $n$  is the electron density and  $f_i$  is the Fermi-Dirac function in region  $i$ . In this tunneling process, an initial state in region  $l$  must be occupied ( $f_l$ ), and a final state in region  $m$  must be empty ( $1 - f_m$ ). The tunneling probability  $T_t$  is evaluated with the Wentzel-Kramers-Brillouin approximation [14]. The summation is taken with respect to momentum for all electrons satisfying the conservation relations Eqs. (2) and (3) under the bias condition Eq. (1) in the context of two different metals. The final tunneling current density  $J(V, z)$  is given as the difference between tunneling current components from CNF to Au and from Au to CNF. Therefore,

$$J(V, z) = J_{Au \leftarrow CNF} - J_{CNF \leftarrow Au}. \quad (5)$$

Equation (5) is evaluated numerically by changing the momentum summation to integration with respect to transverse momentum  $k_{\parallel}$  and total energy  $E$ .

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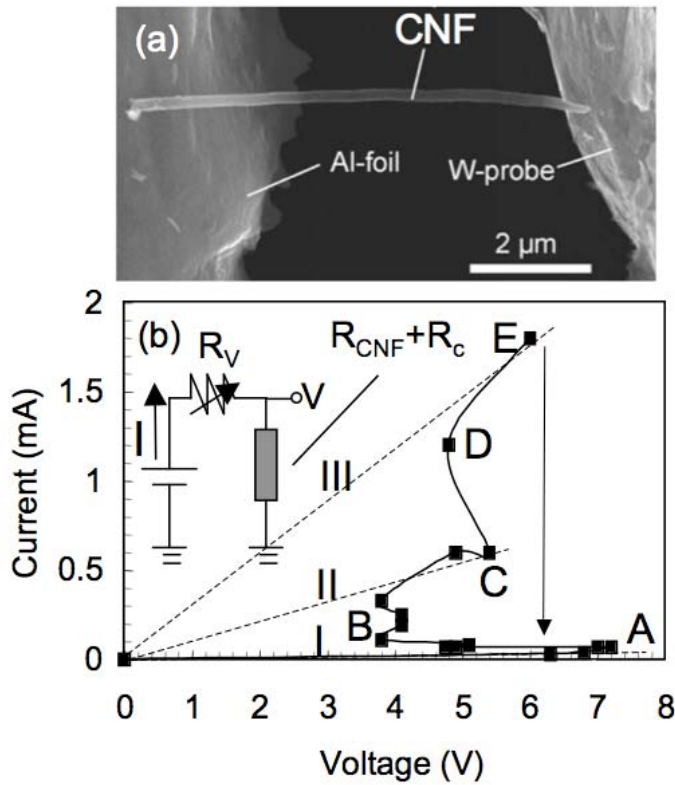


Figure 1. (a) SEM image of a CNF suspended in vacuum with Al and W electrodes. (b) Measured  $I$ - $V$  for the suspended CNF, whose electrodes are connected to battery and variable resistor in series. In general,  $R_V \gg R_c + R_{CNF}$ .

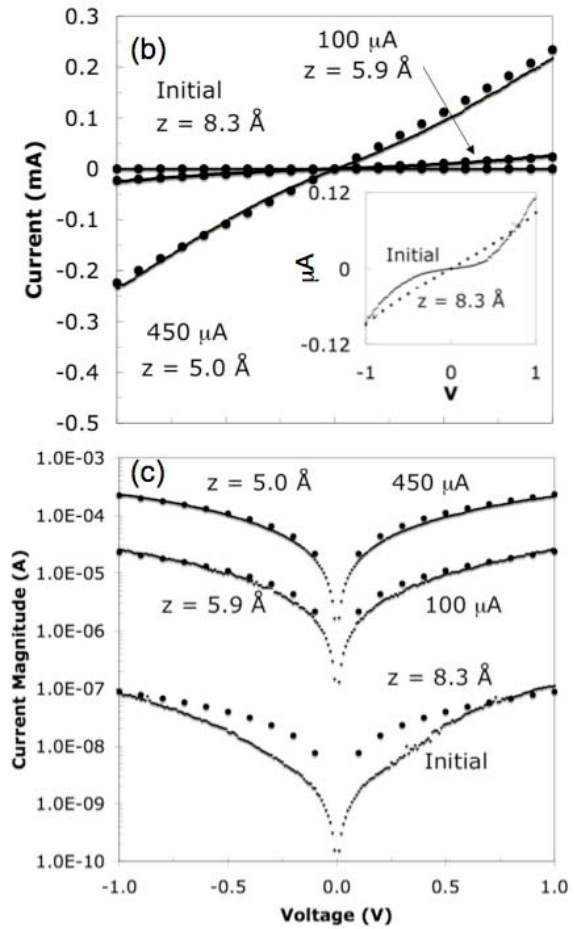


Figure 2. (a) SEM image of a CNF bridging two Au electrodes on  $\text{SiO}_2$  substrate. (b)  $I$ - $V$  behaviors before and after current stressing cycles: the first by 100 μA and the second by 450 μA. Solid circles represent model results.  $z$  values of 8.3, 5.9, and 5.0 Å provide the best fit between experiment and model. (c) Semi-log plot of (b).

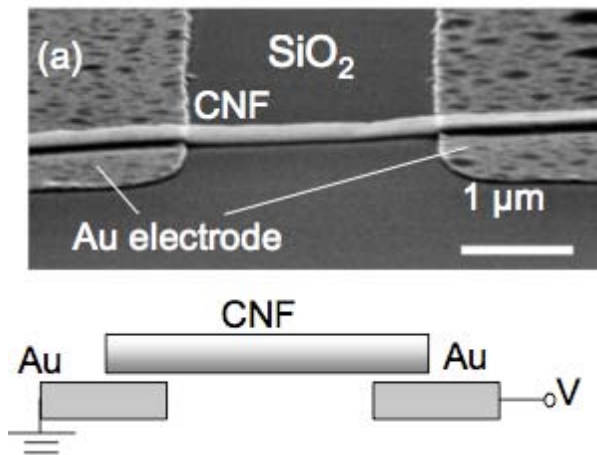


Figure 3. Energy band model for Au-vacuum-CNF tunneling junction with energies in units of eV. CNF is biased at  $V$  with respect to Au, and tunneling current  $I$  flows from CNF to Au.