Current anisotropy of carbon nanotube diodes: Voltage and work function dependence

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Here, we report a performance analysis on carbon nanotube (CNT) Schottky diodes using source-drain current anisotropy. An analytical model is derived based on thermionic field emission and used to correlate experimental data from Pd–Hf, Ti–Hf, Cr–Hf, Ti–Cr, and Pd–Au mixed metal devices fabricated on one single 6 mm long CNT. Results suggest that the difference in work functions of the two contact-metals, and not a dominant Schottky contact, determines diode performance. Results are further applied and demonstrated in a reversible polarity diode. © 2010 American Institute of Physics. [doi:10.1063/1.3458818]

With implementation of carbon nanotubes (CNTs) into steadily more advanced logic circuits,1–4 advances in growth and positioning,5–8 and better contact engineering,9–13 scalable CNT-based logic circuits could be feasible within the next decade. CNT-based Schottky diodes are of particular interest due to simple fabrication and promising high-frequency characteristics.14 Hence, the literature is littered with individual diode devices utilizing mixed-metal contacts to CNT.14–18 The diode-like characteristics of these mixed-metal devices is suggested to result from one contact having Ohmic properties (typically Pd or Ti) and the other being Schottky in nature. Intrinsically, this assumes that the energy difference between the contact-metal work function (Φm) and CNT Fermi level (EF) determines the device current-rectifying ability. However, the validity of this assumption has not been systematically tested and no model has been developed to explain the Φm-dependent rectifying capabilities.

Using experimental data fitted to a derived theoretical model, we demonstrate that in hole-conducting devices where both contacts are Schottky in nature, the difference in Φm (ΔΦm=Φm1−Φm2) determines the rectification, not the energy band alignment at a dominant Schottky contact. This result is applied to demonstrate a reversible polarity diode with bias-dependent rectifying characteristics.

To construct a model for CNT diode hole transport with gate-bias Vg=−15 V, we introduce current anisotropy defined by

\[ \text{Anisotropy} = \left| \frac{I_{FD}}{I_{RD}} \right| \]

where Isd is the larger magnitude current (Vsd>0 for consistency). Note, that this definition does not imply direction of current flow as in a typical metal–semiconductor junction. Here, I_R is the smaller magnitude current (Vsd<0 V) and I_F the larger current (Vsd>0). For a mathematical model of Α, a few assumptions are needed as follows: (i) both metal contacts to the CNT are Schottky in nature. (ii) For I_F (I_R), the contact with larger (smaller \( \Phi_m=\Phi_m2 \)) \( \Phi_m=\Phi_m1 \) is the dominant contact. The large work function \( \Phi_m1 \) (small \( \Phi_m2 \)) contact will be defined by Schottky barrier height \( \Phi_{b1} (\Phi_{b2}) \) with subscript “1” (2), and (iii) application of \( V_g=−15 \) V is sufficient to bias the device in the hole-only conducting state for all devices/metals.

Assumption (ii) is most significant, since it presents a new paradigm for on-state hole transport in CNT diodes. By assuming a \( V_{sd} \) dependent dominant contact, we effectively propose that the resistance of current entering the CNT from the metal at either contact is less than that from the CNT channel to the metal (for both contacts and metal type independent). Although contrary to three-dimensional semiconductors, this assumption is appropriate for CNT due to the large tunneling current contribution to current flow from the metal to the semiconductor. The assumption is visually explained by the band diagrams in Figs. 1(a) and 1(b).

To verify the above hypotheses, we introduce a model utilizing the above assumptions derived from thermionic...
field emission (TFE), and fit the model to experimental observations. TFE was chosen since in its limiting conditions, it accurately models both field emission and thermionic emission. As mentioned above, assuming that $\Phi_{b2}$ is dominant for hole transport $I_g$ and $\Phi_{b1}$ is dominant for hole transport $I_F$, we have the following expressions for the magnitudes of $I_F$ and $I_g$:

$$|I_{F(i=1),R(i=2)}| = \frac{A \pi^{1/2}E_{00}^{1/2}(\Phi_{b(i)} - |V_{sd}| + s_{i(i)})^{1/2}}{kT \cosh(E_{00}/kT)}$$

$$\times e^{(s_{i(i)} \Phi_{b(i)} + s_{i(i)})/(e^{V_{sd}/kT} - 1)} .$$

(1)

where $T$ is temperature (kelvin), $A$ is the Richardson constant, $k$ is the Boltzmann constant, $\xi_2 = E_f - E_v = 0$ for $V_g = -15$ V ($E_v$-CNT valence band), $E_{00}$ is a TFE tunneling parameter, and $E_{00} = E_{00} \coth(E_{00}/kT)$. Applying the above with the Schottky–Mott relationship $\Phi_b = \Phi_s - \Phi_m^{20}$ substituting into Eq. (1), and solving for $\tilde{A}$ using a first order linear approximation:

$$\ln(\tilde{A}) \propto \Phi_{b2} - \Phi_{b1} \propto -\Delta \Phi_m .$$

(2)

To test the model, a single 10 mm long thermal chemical vapor deposition-grown CNT was contacted with metals Hf, Cr, Ti, Au (Au with 3 nm Ti adhesion layer), and Pd on a Si/SiO$_2$ wafer, using an e-beam lithography and liftoff method (see Ref. 12 for similar device figure). Since devices were fabricated on the same CNT, fabrication is more difficult but we may assume a consistent CNT band gap, resistance, fabrication/growth conditions, and environment. These are all necessary assumptions to accurately validate the derived TFE model, as use of different CNT will vary each of the parameters. $I$-$V$ measurements were performed in ambient using a probe station with $V_g$ applied via a back gate, unless otherwise noted. $\tilde{A}$ was then calculated point by point for the following metal electrode pairs: Hf–Cr, Hf–Ti, Hf–Pd, Cr–Ti, Pd–Au. Ambient $\Phi_m$ used in the remainder of this report are as follows: Hf=4.0, Cr=4.4, Ti=4.6, Au=4.8, and Pd~4.9–5.0. We first consider the Pd–Hf device measured in ambient and then vacuum as in Fig. 1(c). Devices fabricated with Pd and Hf contacts had the largest $\Delta \Phi_m$ and largest $\tilde{A}$, as in Fig. 1(d). Three following effects are evident from Fig. 1: (i) $I_g$ decreases by an order of magnitude when comparing measurements in air and vacuum. This is a direct result of the Pd $\Phi_m$ increase and Hf $\Phi_m$ decrease due to gas desorption in vacuum. (ii) $\tilde{A}$ is exponentially related to $V_{sd}$. (iii) $\tilde{A}$ of the Pd–Hf device in the vacuum state is significantly increased when compared to ambient; for $V_{sd} = \pm 0.5$ V, anisotropy increases from $\tilde{A} = 10$ in ambient to $\tilde{A} = 55$ in vacuum without device modification.

To expand upon the qualitative $\Phi_m$ dependence in the Pd–Hf results, other mixed-metal devices measured from the same 6 mm long CNT are plotted and fit with Eq. (2). Figure 2(a) displays the raw $\tilde{A}$ for different hybrid device types. Each curve was produced via point by point averaging of three to five different devices.

Figure 2(a) shows that as $\Delta \Phi_m$ increases, $\tilde{A}$ increases for significantly large $V_{sd}$ (≈0.5 V). To fit Eq. (2), we plot $\ln(\tilde{A}) \propto \Phi_{b2} - \Phi_{1b}$ at $V_{sd} = 0.5$ V in Fig. 2(b). $\Phi_{1b,2}$ were found by assuming $X_{CNT} = 4.5$ eV (graphite), and $E_g = 0.65$ eV for a CNT with diameter of 1.7 nm, giving $\Phi_b = 5.15 - \Phi_m$. The resulting graph of $\ln(\tilde{A})$ in Fig. 2(b) is fit well to Eq. (2). If intrinsic $\Phi_m$ values for the vacuum measurement of the Hf–Pd device are assumed (Hf=3.9 eV, Pd=5.2 eV), the resulting data point also fits well to the best fit of Eq. (2), further reassuring the validity of the TFE model and the three major assumptions. Further, the best-fit line has slope $E_{00} = 0.285$, suggesting field emission is dominant for hole on-state transport.

Next, we examine the effect of $V_g$ and majority carrier on a Pd–Hf device. Figure 3(a) displays $I_{sd}$ versus $V_{sd}$ for a mixed-metal device in following three gate-bias regimes: $V_g = -20$ V is a hole-conducting diode, $V_g = -8$ V corresponds to a resistor, and $V_g = 16$ V is an electron transport diode. In the hole conducting on state shown in Fig. 3(b) the device displays $\tilde{A} = 10$, while the resistor state has $\tilde{A} = 1$. At

![FIG. 2.](image-url) Mixed-metal devices on 1.7 nm diameter CNT: (a) average $\tilde{A}$ vs $V_{sd}$ for three to five devices of each pairing. (b) $\ln(\tilde{A})$ vs $\Phi_{2b} - \Phi_{1b}$ with best fit. Inset shows linear plot of $\tilde{A}$ vs $\Phi_{2b} - \Phi_{1b}$.

![FIG. 3.](image-url) Reversible polarity diode: (a) $|I_{sd}|$ vs $V_{sd}$ for $V_g = 16$, $-8$, and $-20$ V. (b) $\ln(\tilde{A})$ vs $V_g$ at $V_{sd} = 0.5$ V.
\[ V_g = 16 \text{ V}, \text{ the device has } \Delta = 0.1. \text{ Equation (2) can be re-written for electron transport in the form } \ln(\Delta) \propto (\Phi_{b2} - \Phi_{b1}). \text{ If it is further assumed that } \Phi_{b2} = \Phi_{m1} - \left[ 4.5 + 0.5E_F e^{-V_g/\tau} \right] \text{ for electrons, } x \in \{1, 2\}, 0 \leq V_g, \text{ and } \tau \text{ a constant dictated by } V_g \sim E_F \text{ coupling strength, it can be shown that:} \]

\[ \frac{\partial \ln(\Delta)}{\partial V_g} \propto -V_g. \tag{3} \]

This equation is equivalent to the hole-only relationship, valid only for single carrier type conduction for large \( \pm V_g \) as in Fig. 3(b). Figure 3(b) also indicates that although the device changes polarity, the current magnitude in the intermediate resistor state is by far the greatest. Also, for \( V_g \gg 0 \), \( I_{sd} \) is small for either \( \pm V_{sd} \) while \( I_{sd} \) at \( V_{sd} < 0 \) (on state) at \( V_g = 16 \text{ V} \) is actually lower than \( I_{sd} \) for \( V_{sd} < 0 \) (off state) at \( V_g = -16 \text{ V} \); limiting practical utilization of the device.

In summary, we have demonstrated that in CNT-based Schottky diodes, the primary variable in controlling rectification capabilities is \( \Delta \Phi_{m2} \) between the mixed-metal contacts. The CNT-based reversible polarity device, although having reduced current anisotropy compared with Si planar diodes, has greater versatility. A circuit based on adaptive reversible polarity diodes may be implemented in both pull-up or pull-down networks without physical modification.

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