# Modeling of kink-shaped carbon-nanotube Schottky diode with gate bias modulation

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A model is proposed for the recent gate voltage $V_G$ modulation experiment of a kink-shaped carbon nanotube (NT) Schottky diode [Z. Yao, H. Postma, L. Balents, and C. Dekker, Nature (London) **402**, 273 (1999)]. Since larger $V_G$ increases both the forward and the reverse turn-on voltages of the diode, we show that: (1) the rectification must occur at the kink where the metallic and the semiconducting NTs meet, and not at the electrode contact, and (2) the semiconducting NT must be *n* type. The turn-on voltages are derived analytically as a function of $V_G$ considering the electrode contact contribution and a good agreement is obtained with the experimental data. *© 2002 American Institute of Physics.* [DOI: 10.1063/1.1481213]

Recently, the Delft group has observed rectifying current–voltage characteristics for a fused kink-shaped carbon nanotube (NT) metal–semiconductor (MS) diode.[1] They applied the gate voltage $V_G$ to change the carrier density in the semiconducting NT and modulated the diode characteristics. Previous analysis focused on the two-terminal properties with a one-dimensional (1D) coherent transport model in a self-consistent field.[2] In this letter, we will emphasize the three-terminal properties, i.e., how $V_G$ modulates the diode characteristics. From this $V_G$ dependence, we show that: (1) the rectification occurred at the NT MS junction and not at the electrode contact, and (2) the carriers involved in the transport must be electrons rather than holes, unlike commonly observed *p*-type NTs.

In Ref. 1, they placed NTs on TiAu electrodes on a $SiO_2$/doped-Si substrate (backgate) as in Fig. 1(a) and applied $V_G$ to the backgate with electrode 3 grounded under a low temperature environment of 100 K. The circuit between electrodes 0 and 1 showed linear characteristics (110 kΩ) without noticeable $V_G$ dependence. Thus, the left NT was metallic. However, the circuit between electrodes 1 and 3 across 2 showed rectifying characteristics with appreciable $V_G$ dependence as in Fig. 1(b). Therefore, the right NT had to be semiconducting. We introduce an equivalent circuit with drain current $I_D$ and voltage $V_D$ at electrode 1. A linear resistor $R_1$ represents contact 1. $V_G$ modulates the carrier density in the semiconducting NT and a capacitor $C_{NT}$ represents the capacitance with respect to the substrate. The metallic and the semiconducting NTs meet at kink 2, and a MS junction $J_2$ is formed. The semiconducting NT reaches electrode 3 and a semiconductor–metal (SM) junction $J_3$ is formed. For rectification to take place, either $J_2$ or $J_3$ should be a Schottky diode and the other should be a resistive element. In fact, if both are Schottky diodes, then $J_2$ and $J_3$ are either front-to-front (-|>|-|<|-) or back-to-back (-|<|-|>|-) connected by sharing the semiconducting NT and will allow only negligible current through them. If both are resistive elements allowing current in both polarities, then there is no mechanism for rectification.

The forward direction occurred when $V_D > 0$.[1] Thus, two equivalent circuits are possible: $J_2$ is a Schottky diode with an *n*-type NT and $J_3$ is a resistor as in Fig. 2(a), or $J_2$ is a resistor and $J_3$ is a Schottky diode with a *p*-type NT as in Fig. 2(b). We introduce forward and reverse turn-on voltages for a diode, $V_{onF}$ and $V_{onR}$, respectively,[3] corresponding to the onset of $I_D$. The experimental $V_G$ dependence is such that: if $V_G < V'_G$, then $0 < V_{onF} < V'_{onF}$ and $V_{onR} < V'_{onR} < 0$ as in Fig. 1(b), where a prime indicates a quantity at $V'_G$. Or increasing $V_G$ shifts both $V_{onF}$ and $V_{onR}$ in the positive $V_D$ direction.

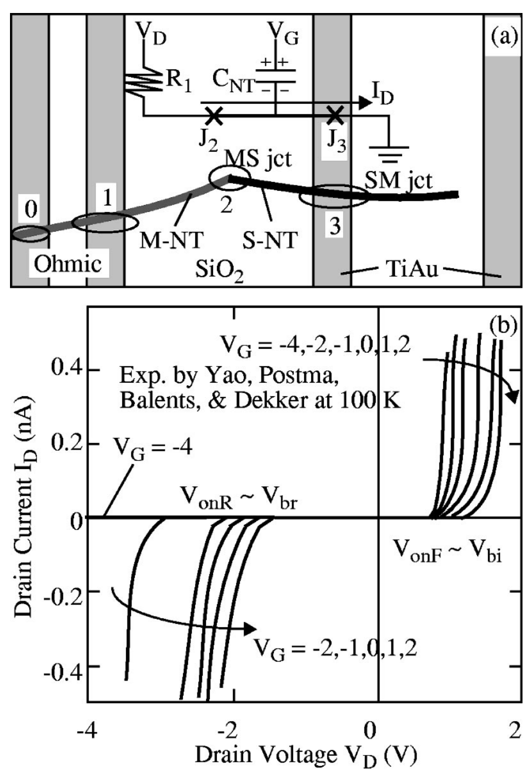


FIG. 1. (a) Experimental setup and its equivalent circuit; (b) $I_D - V_D$ characteristics between electrodes 1 and 3 with $V_G$ as a parameter at 100 K (experiment by Yao *et al.*, Ref. 1).

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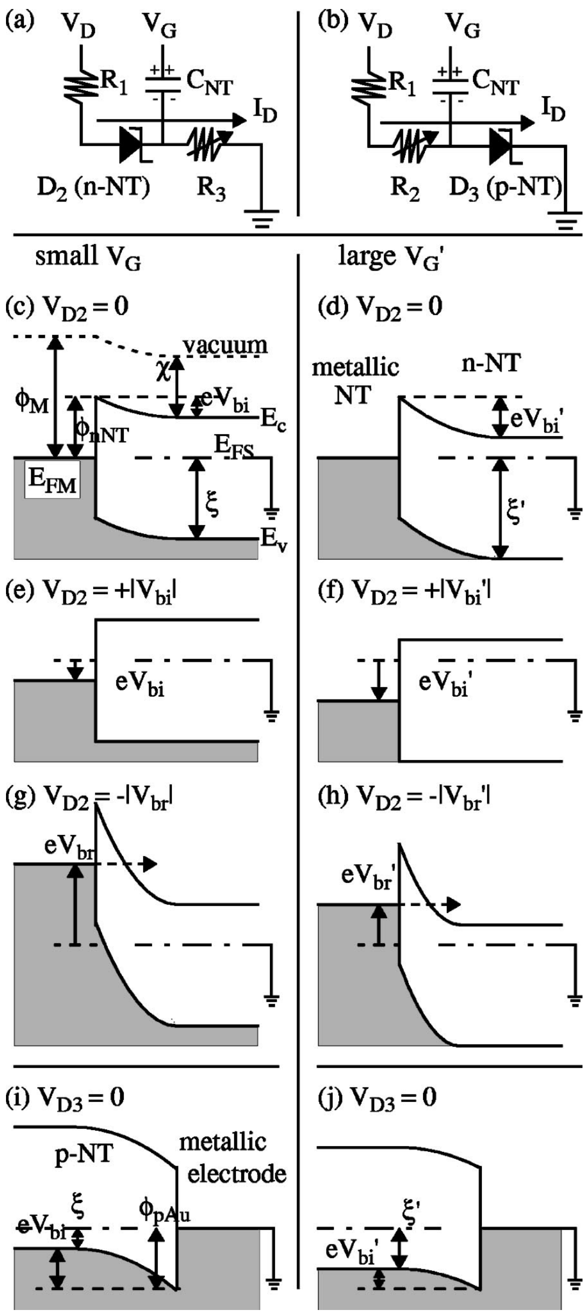


FIG. 2. Rectification mechanisms: (a) equivalent circuit with a fused NT MS junction $D_2$ of $n$ type and an ohmic contact $R_3$ with a capacitor $C_{\rm NT}$; (b) equivalent circuit with an ohmic contact $R_2$ and an NT–electrode SM junction $D_3$ of $p$ type; (c)–(h) energy band diagrams for selected $V_{D2}$s in the $n$-NT scenario of (a); (i)–(j) energy band diagrams for $V_{D3}=0$ in the $p$-NT scenario of (b). Small $V_G$ (left) and large $V_G'$ (right) cases are examined, where $\phi_M$ is a work function, $\phi_{n\rm NT}$ and $\phi_{p\rm Au}$ are Schottky barriers, $E_{\rm FM}$ and $E_{\rm FS}$ are electrochemical potentials, $\xi$ is a chemical potential, $E_c$ and $E_v$ are conduction and valence band edges with a band gap $E_g$, $V_{\rm bi}$ and $V_{\rm br}$ are built-in and breakdown voltages, and $\chi$ is an electron affinity.

Such $V_G$ dependence is possible with an $n$-NT, but not with a $p$-NT. The band diagrams for Schottky diode $D_2$ of $n$ type in Fig. 2(a) are shown in Figs. 2(c)–2(h) for selected $D_2$ voltages $V_{D2}$s, and those for $D_3$ of $p$ type in Fig. 2(b) are shown in Figs. 2(i)–2(j) for null $D_3$ voltage $V_{D3}$, respectively. We compare small $V_G$ (left) and large $V_G'$ (right) cases. $\phi_M$ is a metallic NT work function. $\phi_{n\rm NT}$ and $\phi_{p\rm Au}$ are Schottky barriers for electrons at $D_2$ and holes at $D_3$, respectively. $E_{\rm FM}$ and $E_{\rm FS}$ are electrochemical potentials (Fermi levels) in the metallic and the semiconducting NTs. $E_c$ and $E_v$ are conduction and valence band edges with a band gap $E_g$. $\xi$ is a chemical potential $E_{\rm FS}-E_v$ and $\chi$ is an electron affinity. $V_{\rm bi}$ ($>0$) is a built-in voltage and $V_{\rm br}$ ($<0$) is a breakdown voltage. $e$ ($>0$) is the unit charge.

We examine the $n$-NT scenario with $D_2$ as in Fig. 2(a) and compare the influences of $V_G$. Increasing $V_G$ results in higher electron density, and $\xi$ increases. Thus, $\xi<\xi'$ and we may think that the doping is effectively increased. Since $\phi_{n\rm NT}$ is independent of $V_G$, $V_{\rm bi}<V_{\rm bi}'$ as shown in Figs. 2(c) and 2(d). In the thermionic emission[3] (Ref. 2 estimated a thick Schottky barrier of several nanometers), the forward turn-on occurs when $V_D\sim V_{\rm bi}$. Therefore, $V_{{\rm on}F}<V_{{\rm on}F}'$, as in Figs. 2(e) and 2(f). This is consistent with the experiment. The reverse turn on occurs when the gradient and the width of the Schottky barrier exceed certain thresholds or $V_D\sim V_{\rm br}=-|V_{\rm br}|$. This is the beginning of the tunneling breakdown. The effective doping is larger for larger $V_G$, leading to the thinner Schottky barrier as in Figs. 2(g) and 2(h). Thus, $-|V_{\rm br}|<-|V_{\rm br}'|$ and $V_{{\rm on}R}<V_{{\rm on}R}'$. This is also consistent with the experiment.

However, neither trends for $V_{{\rm on}F}$ and $V_{{\rm on}R}$ are explained by the $p$-NT scenario with $D_3$ as in Fig. 2(b). Increasing $V_G$ results in lower hole density and $\xi$ increases. Thus, again $\xi<\xi'$. However, $V_{\rm bi}>V_{\rm bi}'$ for holes as shown in Figs. 2(i) and 2(j). Thus, $V_{{\rm on}F}>V_{{\rm on}F}'$ in the forward direction, but this is contrary to the experiment. In the reverse direction, the effective doping is smaller for larger $V_G$ and the Schottky barrier is thicker. Thus, $-|V_{\rm br}|>-|V_{\rm br}'|$ and $V_{{\rm on}R}>V_{{\rm on}R}'$. This is again contrary to the experiment. Therefore, we conclude that: (1) the rectification occurred at $D_2$, and (2) the NT must be $n$ type.

We will express $V_{{\rm on}F}$ and $V_{{\rm on}R}$ as a function of $V_G$ based on this view. Since the onset of $I_D$ is our present interest, we do not solve the transport problem but identify the diode turn-on voltages. This is practically enough for many electronics applications.[3,4] $V_G$ attracts or repels electrons through contact 3 (electrodes are infinite charge reservoirs), and causes a linear change in $\xi$, such that $\xi(V_G)=\xi(0)+\alpha eV_G$. The coefficient $\alpha$ is related to the NT state density and $C_{\rm NT}$,[5] and thus depends on the quasi-1D NT band structure as well as the detailed device geometry including the $SiO_2$ layer. The NT specific information is embedded in $\alpha$. By inspecting the band diagram in Fig. 2(c), we have $eV_{\rm bi}=\phi_{n\rm NT}-[E_g-\xi(V_G)]$. The forward turn on is achieved by applying $V_{D2}=V_{\rm bi}$. Thus, the forward turn-on modulation by $V_G$ is given by $\Delta V_{\rm bi}(V_G)=\alpha\Delta V_G$.

The reverse turn on for a different $V_G$ occurs when the Schottky barrier has the same slope (electric field) at the junction. In this case, transport electrons see the same Schottky barrier height and the width since $\phi_{n\rm NT}$ is independent of $V_G$. The electric field at the junction is proportional to $[(V_{\rm bi}+|V_{\rm br}|)N_d^+]^{1/2}$ based on the planar junction theory.[3] By equating $(V_{\rm bi}+|V_{\rm br}|)N_d^+$ for finite and zero $V_G$ cases with an ionized donor density $N_d^+$, we have $(V_{\rm bi0}+|V_{\rm br}|-\alpha V_G)(N_{d0}^+ +N_{d0}^+V_G/\beta)=(V_{\rm bi0}+|V_{\rm br0}|)N_{d0}^+$, where the subscript 0 refers to $V_G=0$. $V_G=-\beta$ ($<0$) is a voltage such that the electrons are repelled completely, and the NT becomes intrinsic. The reverse turn on is achieved by applying $V_{D2}=V_{\rm br}$. Therefore, the modulation is given by $\Delta V_{\rm br}(V_G)=-(|V_{\rm br}|-|V_{\rm br0}|)=\alpha\Delta V_G-\Delta[(V_{\rm bi0}+|V_{\rm br0}|)/$

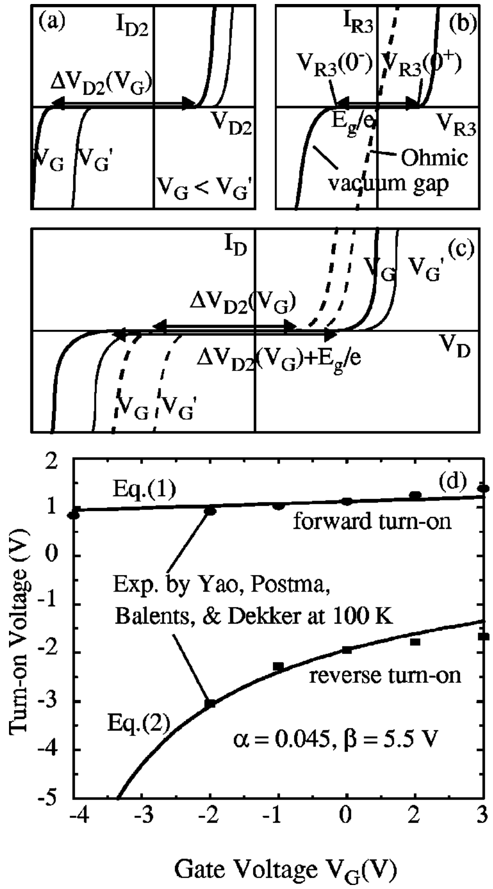


FIG. 3. Comparison to experiment: (a) schematic $I_{D2}-V_{D2}$ characteristics for Schottky diode $D_2$ with two gate biases $V_G$ (thick line) $< V_G'$ (thin line); (b) schematic $I_{D3}-V_{D3}$ characteristics for SM contact $R_3$ with vacuum-gap (solid line) and ohmic (dotted line) modes; (c) schematic $I_D-V_D$ characteristics for the entire circuit with two gate biases and two contact modes; (d) comparison of Eqs. (1) and (2) to experimental $V_{\mathrm{on}F}(V_G)$ (circles) and $V_{\mathrm{on}R}(V_G)$ (squares) at 100 K.

$(1+V_G/\beta)]$. The term $\alpha V_G$ appears in both $\Delta V_{\mathrm{bi}}$ and $\Delta V_{\mathrm{br}}$ since it represents the same effect of $V_G$ upon $\xi$.

Practically, $V_{D2}$ cannot be directly measured due to the electrode contacts. In Ref. 1, $R_1$ was about a half of 110 k$\Omega$ and can be safely neglected, but $R_3$ cannot be. Figures 3(a) and 3(b) show current–voltage characteristics $I_{D2}-V_{D2}$ for $D_2$ and $I_{R3}-V_{R3}$ for $R_3$, respectively. Then, $I_D = I_{D2} = I_{R3}$ and $V_D = V_{D2} + V_{R3}(I_D)$ appear finally as in Fig. 3(c). If $R_3$ is ohmic (dotted line), $V_{R3}(0^+) = V_{R3}(0^-) = 0$ and the final $I_D$-absent domain remains the same, $\Delta V_{D2}$. However, if $R_3$ has the "vacuum-gap"[6] characteristics (solid line), $V_{\mathrm{on}F}$ and $V_{\mathrm{on}R}$ are offset by $V_{R3}(0^+)$ and $V_{R3}(0^-)$, respectively, where $V_{R3}(0^+) - V_{R3}(0^-) = E_g/e$. Thus, the final $I_D$-absent domain is $\Delta V_{D2} + E_g/e$. Since the experimental $V_{\mathrm{on}F} = 0.8-1.4$ V[1] was somewhat beyond the theoretical $E_g/e = 1.2$ V for (7,1)/(8,0) kink-shaped MS NT,[7] we assume the "vacuum-gap" mode for $R_3$. In fact, the $I_D$-absent domain is pronounced at lower temperatures[8] and this is consistent with the measurement at 100 K.[1] The turn-on voltage modulation by $V_G$ including the $R_3$ contribution is given by

$$V_{\mathrm{on}F}(V_G) = V_{\mathrm{on}F}(0) + \alpha V_G, \tag{1}$$

$$V_{\mathrm{on}R}(V_G) = V_{\mathrm{on}R}(0) + \alpha V_G + (V_{\mathrm{on}F}(0) + |V_{\mathrm{on}R}(0)| - E_g/e) V_G/(\beta + V_G), \tag{2}$$

where the partition of $E_g/e$ for $V_{\mathrm{on}F}(0)$ and $|V_{\mathrm{on}R}(0)|$ does not have to be known. Equations (1) and (2) are now ready for experimental comparison. They will be extended for other gated MS diode analysis, with an appropriate inclusion of the contact contributions.

We have chosen $\alpha = 0.045$ and fitted Eq. (1) to the experimental $V_{\mathrm{on}F}(V_G)$.[1] With a choice of $\beta = 5.5$ V (compatible with the negligible reverse $I_D$ at $V_G = -4.0$ V),[1] Eq. (2) recovers the experimental $V_{\mathrm{on}R}(V_G)$ quite well as in Fig. 3(d), and this gives the foundation for our modeling. Quasi-1D junction field[9] and image potential[3] effects would not be relevant and are not included in our model, but they could be necessary in the analysis for finite $I_D$.

Although the present NT must be *n* type, NTs have been *p* type in many cases.[10] Several mechanisms have been proposed for this *p*-type behavior, and oxidation in air is one of them. The thermoelectric experiments showed that NTs are originally *n* type due to unintentional doping in the production process, but turn to *p* type after the air oxidation.[11,12] The oxidation typically occurs on the order of hours at 300 K with the binding energy of the adsorbed oxygen $\sim$5000 K.[12] Thus, at 100 K, the oxidation is significantly suppressed ($e^{-5000/100}/e^{-5000/300} \sim 3\times10^{-15}$), and this could be a possible mechanism for the *n* type here. The trapped charges in or on the $SiO_2$ layer[3] might have contributed to the *n*-type behavior. The apparent difference of the present fused MS NT compared to the previous all semiconducting NTs may also be relevant.

In summary, Delft's gated NT MS diode measurements are studied. It is shown that the rectification occurred at the kink of the NT junction and the NT must be *n* type. We have derived turn-on voltages $V_{\mathrm{on}F}$ and $V_{\mathrm{on}R}$ as a function of $V_G$ analytically, and recovered the experimental data well.

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[4] This is similar to the role of a turn-on voltage 0.7 V for a typical Si $p-n$ junction diode.
[5] $V_G$ induces charges $-C_{\mathrm{NT}}V_G$ in the NT, and this is converted to $\Delta\xi$. Thus, $\alpha \sim C_{\mathrm{NT}}/[C_{\mathrm{NT}} + e^2 D(\xi_0)]$, where $D(\xi_0)$ is a NT state density at $V_G = 0$.
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