Equivalent circuit model for carbon nanotube Schottky barrier: Influence of neutral polarized gas molecules

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(Received 22 August 2005; accepted 5 January 2006; published online 22 February 2006)

An equivalent circuit model is proposed for the Schottky barrier at the junction between a metallic electrode and a semiconducting carbon nanotube (NT). We have applied the model to a gold-NT junction under the presence of neutral polarized NH_3 molecules, and have shown that visible Schottky barrier modulation is possible for the gas densities as low as 3×10^{13} cm^{-2}, which is quite feasible experimentally. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2177356]

Carbon nanotube (NT) field-effect-transistors (FETs) (Ref. 1) garner much attention because the drain current changes by orders of magnitude in the presence of gases, such as NH_3, NO_2, O_2, etc.[2,3] These gases generally modulate NT-electrode contact properties (Schottky barrier)[4] and/or NT bulk properties (Fermi level).[5]

O_2 will enhance hole transport in *p*-NT FETs and increase the drain current. The FET experiments showed that O_2 modulates the NT Schottky barrier rather than the NT bulk Fermi level.[3] While earlier theoretical work suggested that the NT-O_2 interaction would lower the NT Fermi level (*p* doping),[6,7] recent work indicates that little charge transfer occurs (no doping).[8–10] However, Schottky barrier modulation is still possible when O_2 molecules are present between the electrode and NT, and are charged.[11]

Generally, charged gas molecules can modify the Schottky barrier. Let us assume that the metal-gas interaction is strong. The electrode surface will be atomically rough with clusters and there will be a gap[11] between the electrode and NT as shown in Fig. 1(a). In the open-circuit condition, positive charges can appear only in the metal as shown in Fig. 1(b). In the closed-circuit condition, however, the positive charges are redistributed through the conduction line and can also appear in the NT as shown in Fig. 1(c). This determines the NT Schottky barrier in the practical experimental situations.[11]

NH_3 will weaken hole transport in *p*-NT FETs and reduce the drain current.[2,12,13] Early theoretical studies predicted that the NT-NH_3 interaction would raise the NT Fermi level (*n* doping) slightly,[6,14] but recent studies show that no charge transfer will occur between the NH_3 and NT.[15] The charge transfer between the NH_3 and gold is also shown negligible,[16] and the molecules stay neutral. The existence of *n* doping by NH_3 was discussed in the experiments,[12,13] but it is challenged by the possible existence of water in the environment.[16] The only unanimous conclusion available at this stage on the NH_3 electrostatic properties is that the molecules are inherently polarized, and they have a preferred dipole direction with respect to the electrode gold surface.[16]

Here, we propose an equivalent-circuit model and show how neutral polarized molecules can still modify the electrode-NT Schottky barrier with a feasible gas coverage density. The open- and closed-circuit conditions will again bring about different electrostatics in the gap. We assume that the polarized molecules will have a preferred orientation in the gap as indicated in Fig. 1(d). Positive and negative charges will appear in the metal and NT in the closed-circuit condition to compensate for the work-function difference. As a result, a gap field is created. If the gap field is along the polarization as shown in Fig. 1(e), the dipole alignment is stable. If not, the dipoles may flip as shown in Fig. 1(f).

Figure 2(a) shows the band diagram at the junction between the metal and *n*-NT. $\Delta U(>0)$ is the potential drop from the metal to the NT in the gap, and ϕ_0 (>0) is the band bending at the end of the NT. They will be negative if the energy directions are opposite. The gas molecules can modify both of them, while the following quantities, the metal work function χ_m, the NT electron affinity ϕ_s, and the NT Fermi level ζ stay unchanged and are positive. Then, the Schottky barrier for electrons Φ_{Be} is obtained as a voltage of the node between ϕ_s and ϕ_0, and that for holes Φ_{Bh} is given by $E_g-\Phi_{Be}$, where E_g is the NT band gap. The band diagram shows two critical relations:

$$\chi_m = \Delta U + \phi_s + \phi_0 + \zeta, \tag{1}$$

$$\Phi_{Be} = \phi_0 + \zeta. \tag{2}$$

The charge neutrality relation is satisfied, i.e., $\Sigma Q = Q_m + Q_{\mathrm{gas}} + Q_{\mathrm{NT}} = 0$. Here, Q_m (<0) is the charge on the metal, Q_{gas} is the charge on the molecules (negative for negatively charged molecules and 0 for polar molecules) weighted with the distance from the metal,[5,11] and Q_{NT} (>0) is the charge on the NT. There must be appropriate Φ_{Be} satisfying $\Sigma Q = 0$. In fact, since $\phi_0 = \Phi_{Be} - \zeta$ and ζ is constant, extra large Φ_{Be} will cause large ϕ_0, leading to large Q_{NT} and positive ΣQ. Similarly, extra small Φ_{Be}will cause small ϕ_0, leading to

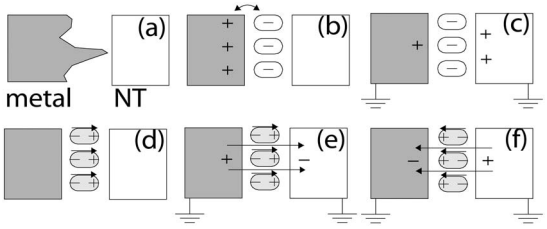

FIG. 1. Metal-NT junction and gas molecules. (a) Rough metallic surface. Charged gas cases in the (b) open- and (c) closed-circuit conditions. (d) Polarized gas case in the open-circuit condition. Polarized gas cases in the closed-circuit condition with (e) supporting and (f) flipping gap fields.

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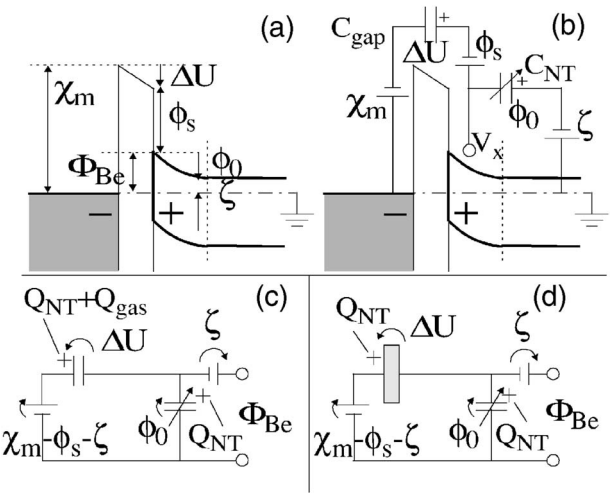

FIG. 2. (a) Band diagram at the metal-NT junction. ΔU (>0) is the potential change and ϕ_0 (>0) is the NT band bending. χ_m is the work function, ϕ_s is the electron affinity, and ζ is the Fermi level. Φ_{Be} is the Schottky barrier for electrons. (b) Straightforward equivalent circuit. Rearranged circuit in (c) the charged gas case and (d) the polarized gas case with voltage polarity reversed.

small Q_{NT} and negative ΣQ. Thus, there is appropriate Φ_{Be} satisfying $\Sigma Q=0$.

In the straightforward equivalent circuit in Fig. 2(b), the band diagram is expressed with batteries and capacitors. C_{gap} is a capacitor corresponding to the gap region. C_{NT} is a nonlinear capacitor reflecting the semiconducting nature of the NT, with accumulation, depletion, and inversion modes. Within each capacitor, the total charges are zero: If one capacitor plate has charge Q, the other must have $-Q$. The problem is mapped to finding a node voltage V_x in the circuit. The potential for electrons is positive in the band diagram, while it is negative in the straightforward circuit. Thus, Φ_{Be} in the straightforward circuit in Fig. 2(b) must be obtained as the magnitude of the node voltage, $|V_x|$.

In the following, we have removed this complication by reversing the voltage definition so that Φ_{Be} should be expressed as the node voltage itself: The potential barrier for electrons is now expressed with a *positive* voltage. Figures 2(c) and 2(d) show rearranged equivalent circuits for the charged unpolarized case and the neutral polarized case, respectively. In the charged case, $\Sigma Q=0$ demands that capacitor C_{gap} have charge $Q_{NT}+Q_{gas}$, and the capacitor C_{NT} have charge Q_{NT}; while in the polarized case, $\Sigma Q=0$ demands that C_{gap} and C_{NT} have the same charge Q_{NT}. In either case, we can recover the critical band relations in Eqs. (1) and (2).

We will study the charge-voltage (Q-V) characteristics of C_{gap} and C_{NT} and find ΔU and ϕ_0. The charge and voltage polarities are defined in the inset of Fig. 3. In a vacuum, C_{gap} will have a linear Q-V relation with the solid line. In charged unpolarized gas, C_{gap} will have a shifted linear relation with the dashed line. This is because the gas molecules simply induce additional charges Q_{gas} and shift the entire vacuum Q-V line by $V=Q_{gas}/C_{gap}$ in the V axis. In the neutral polarized case with a preferred direction, C_{gap} will have the dotted-line characteristics as shown below and large Schottky barrier modulation is expected.

We will consider the gold-NH_3–NT system. In the open-circuit condition, while the NT–NH_3 interaction is negligible,[15] there is a preferred NH_3 dipole direction with respect to the gold surface,[16] as in Fig. 1(d). The preferred

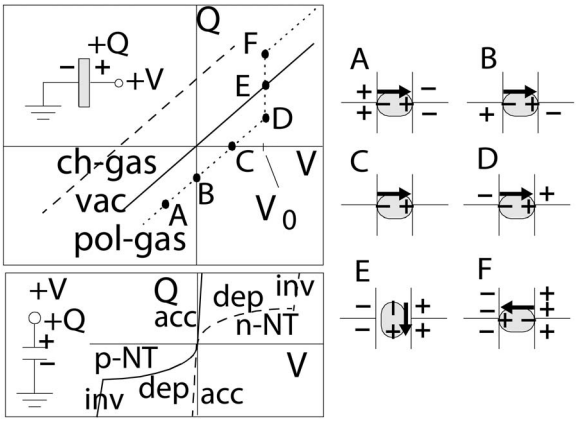

FIG. 3. Top: Characteristics of C_{gap} in a vacuum (solid), charged gas (dotted), and neutral polarized gas (dashed) with gas dipole orientations. Bottom: Characteristics of C_{NT} in the p-NT (solid line) and n-NT (dashed line) cases.

geometry (the nitrogen facing the gold) has a binding energy of −0.32 eV, while the flipped geometry has another binding energy of −0.09 eV in the low coverage limit.[16] The binding energy difference ΔE_b is 0.22 eV. In the closed-circuit condition when NT voltage V with respect to the gold is zero, the positive charge will appear in the gold, and the negative charge will appear in the NT in the absence of NH_3, according to the NT FET experiments at no gate voltage.[3] Thus, the gap field will support the preferred dipole direction for $V=0$ as shown in Fig. 1(e). The right polarization is consistently preferred from negative V_s to a certain positive V_0 as indicated for operating points A–C. The change in V is compensated for by the change in Q as shown in Fig. 3. At $V=V_0$, the dipole μ has an energy of $\mu V_0/\ell=\Delta E_b$, where ℓ is the effective plate distance of C_{gap}. Since D and F have the same energy, a dipole flip is expected. The average dipole $\langle\mu\rangle$ at temperature T and V is given by the Ising spin model, which predicts $\langle\mu\rangle=\mu\tanh[\mu(V-V_0)/\ell k_B T]$ with k_B as the Boltzmann constant.[17] For NH_3, the theoretical study shows that $\mu=0.45$ eÅ near the gold surface, about 40% larger than the free case.[16] Assuming $\ell\sim 3$ Å,[11] we have $V_0\sim 1.5$ V. The transition from D to E to F is rounded because of the thermal energy, slightly by $\ell k_B T/\mu\sim 0.17$ V at 300 K, which is only 10% of V_0. Thus, the transition is considered abrupt enough. The polarization P in the gap is given by $n\mu/\ell$, where n is the surface density of the dipoles. Then $\Delta Q=Q_F-Q_E=Q_E-Q_D=SP$, where S is the plate area. For $V>V_0$, the gap field is strong enough to flip the dipole to the left direction. Thus, the left polarization is consistently preferred. The resultant Q-V characteristics are shown with the dotted line in Fig. 3.

C_{NT} will stay unchanged in gas. The NT has depletion, accumulation, and inversion modes, and its Q-V characteristics are drawn with the solid line for p-NT and the dashed line for n-NT in Fig. 3. The polarity of Q and V are defined as in the inset circuit. For $V>0$, the p-NT is in the accumulation mode and Q rises quickly, while for $V<0$, the p-NT is in the depletion mode and Q is a square root function of V. At large negative V, the p-NT is in the inversion mode and Q becomes large negative quickly. The n-NT behaves in a symmetric manner with respect to the origin, as shown in the figure. The conduction type of NT FETs (or ζ) can be controlled with an application of gate voltage as discussed before.[11]

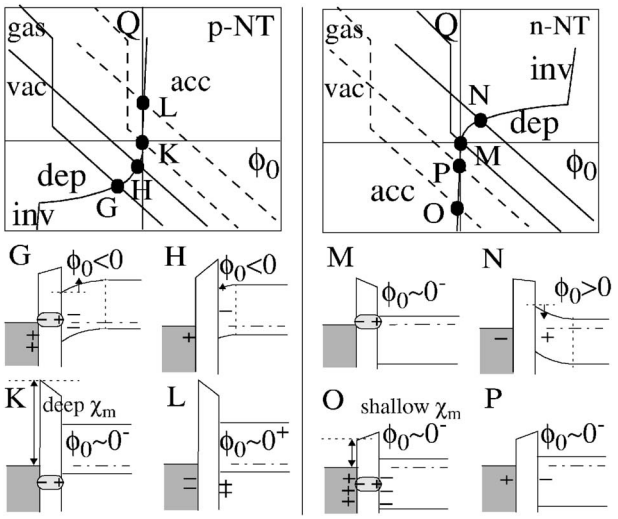

FIG. 4. Left: Load C_{gap} line and C_{NT} line for p-NT. G and H: Large Φ_{Be} (Φ_{Bh}) modulation. K and L: Negligible Φ_{Be} (Φ_{Bh}) modulation. Right: Load C_{gap} line and C_{NT} line for n-NT. M and N: Large Φ_{Be} (Φ_{Bh}) modulation. O and P: Negligible Φ_{Be} (Φ_{Bh}) modulation.

Knowing the Q-V characteristics of C_{gap} and C_{NT}, the original problem of finding Φ_{Be} is reduced to a circuit problem of finding ϕ_0 and Q_{NT} in Fig. 2(d). The load is composed of a battery $\chi_m-\phi_s-\zeta$ and C_{gap} with respect to C_{NT}. Based on the traditional circuit method, we draw Q-V lines for C_{NT} and the load, and then find an intersection. Figure 4 shows the results for p-NT (left) and n-NT (right), respectively.

We will examine the p-NT first. When χ_m is not deep ($\chi_m-\phi_s-\zeta<0$), the vacuum straight loadline has a ϕ_0-axis intersection at $\chi_m-\phi_s-\zeta$ and gives an intersection H, where ϕ_0 is small, negative. The gas kink-shaped loadline gives an intersection G, where ϕ_0 is large negative. Thus, Φ_{Be} is smaller and Φ_{Bh} is larger in gas, leading to poorer hole transport. In the pathological case of extremely deep χ_m ($\chi_m-\phi_s-\zeta>0$), the presence and absence of gas will have intersections K and L, respectively, but ϕ_0 is nearly zero in both cases. Thus, there is practically no Schottky barrier modulation.

The discussion for n-NT can be done in parallel. When χ_m is not shallow ($\chi_m-\phi_s-\zeta>0$), the vacuum intersection N gives large, positive ϕ_0, while the gaseous intersection M gives negligible ϕ_0. Thus, again Φ_{Be} is smaller and Φ_{Bh} is larger in gas. When χ_m is extremely shallow ($\chi_m-\phi_s-\zeta<0$), intersections O and P have negligible ϕ_0 and no Schottky barrier modulation is expected. For large Schottky barrier modulation, it is necessary to involve the NT depletion mode regardless of the conduction type, and this is reminiscent of the charged unpolarized case of O_2.[11]

In order to see visible Φ_{Be} modulation, we require that the voltage at C satisfy $V_{|atC}=\Delta Q\ell/S\epsilon=n\mu/\epsilon\sim E_g/2$, where ϵ is the vacuum dielectric constant and E_g is the NT band gap ($\sim$0.5 eV). This gives $n\sim 3\times 10^{13}$ cm^{-2}, corresponding to only 30 molecules in the area of 100 Å by 100 Å. NH_3 molecules are roughly 1 Å tetragons and this coverage corresponds to only 0.3% of the electrode surface, which is experimentally quite feasible. This gas density is comparable to the gas density of $\sim 10^{13}$ cm^{-2} required for NT Schottky barrier modulation through the charged O_2 molecule mechanism,[11] or the surface state density of $\sim 10^{13}$ cm^{-2} required for Schottky barrier pinning.[18]

As is obvious in Fig. 4, no dipole flip occurs when the depletion mode is involved (no intersection occurs in the second quadrant of the Q-ϕ_0 plot). In the closed-circuit condition with a small drain voltage V_D, the gap field is created so that the preferred right polarization is supported. As long as V_D is small enough compared with V_0, the dipole flip will not occur. Thus, it is critical that the natural gap field direction at $V_G=0$ and $V_D\sim 0$ supports the preferred dipole alignment for large Schottky barrier modulation.

Although the systematic NH_3 dipole alignment at the gold surface is the only electrostatic mechanism, it is not appropriate to interpret that the Schottky barrier modulation is due to the modified gold work function and unmodified NT work function. In fact, since the charges appear in the NT and metal in the closed-circuit condition, we need to interpret that *both* NT and metal work functions are modified. Another way to describe the same situation is that NH_3 dipoles are screened by the charges induced in the NT and metal in the closed-circuit condition, and the Schottky barrier modulation occurs.

In summary, we have proposed an equivalent circuit model for a NT Schottky barrier and have applied the model to NH_3 assuming that the molecules are neutral polarized. The gas density as low as 3×10^{13} cm^{-2} is enough to see visible Schottky barrier modulation.

The author acknowledges helpful discussions with Alessandra Ricca, Charles W. Bauschlicher, Jr., and Geetha Dholakia. The work was supported by Contract No. NAS2-03144 of the University Affiliated Research Center at University of California, Santa Cruz.

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