Modeling of carbon nanotube Schottky barrier modulation under oxidizing conditions

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A model is proposed for the previously reported lower Schottky barrier $\Phi_{bb}$ for hole transport in air than in vacuum at a junction between the metallic electrode and semiconducting carbon nanotube (CNT). We consider the electrostatics in a transition region between the electrode and CNT in the presence or absence of oxygen molecules (air or vacuum), where an appreciable potential drop occurs. The role of oxygen molecules is to increase this potential drop with a negative oxygen charge, leading to lower $\Phi_{bb}$ in air. The Schottky barrier modulation is large when a CNT depletion mode is involved, while the modulation is negligible when a CNT accumulation mode is involved. The mechanism prevails in both $p$- and $n$-CNT’s, and the model consistently explains the key experimental findings.

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I. INTRODUCTION

The effects of carbon nanotube (CNT) oxidation have been studied in thermoelectric experiments, and it has been found that the thermoelectric power coefficient was negative in vacuum and positive in air.1 In fact, the thermoelectric power coefficient indicates how a bulk internal electric field is created in order to counterbalance the bulk carrier flow due to the thermal gradient, and it characterizes the bulk properties.2 Thus oxidation changes the bulk CNT properties.

Recently, oxidation effects have been studied3 using CNT field-effect transistors (FET’s), and it has been shown that the contact properties at the electrode and CNT are modified in oxidation. The CNT was placed on a silicon dioxide layer, and a gate voltage $V_G$ was applied to the doped silicon substrate (backgate) as schematically shown in Fig. 1(a). The CNT was about 1 $\mu$m long, and the source and drain gold electrodes covered about one-third of the CNT, respectively. The channel length was a few tenths of a micrometer. They measured the drain current $I_D$, as a function of $V_G$, and the drain voltage $V_D$, and estimated the channel conductance $g_{d,\mu} = \partial I_D(V_G,V_D)/\partial V_D$. The role of $V_G$ was to change the CNT doping effectively or modulate the Fermi level. With the application of $V_G$, positive and negative charges were introduced as shown in Fig. 1(a). The electric field under the source and drain electrodes was mostly vertical due to the thin CNT and wide electrode geometry. In this situation, the planar junction theory is applicable.5,6 The CNT conduction and valence-band edges have the shape shown in Fig. 1(b) along the arrow path in Fig. 1(a), where $A-D$ indicate spatial points in the structure. The path and electric field are parallel only at the CNT ends, and band bending occurs only there. $V_G$ determines this field strength and, therefore, the amount of band bending. Thus $V_G$ effectively changes the CNT doping and modifies the Fermi level by $\alpha V_G$, where $\alpha$ is related to the oxide capacitance and CNT capacitance.6,7 $\alpha$ is usually on the order of $10^{-1}$ in experiments,3,4 meaning that only a portion of $V_G$ is reflected in the Fermi level change.

In this experimental setup, $g_{d,\mu}$ was observed to rise slowly at a negative $V_G(V_{G1})$ and rapidly at a positive $V_G(V_{G2})$ in vacuum as indicated in Fig. 2(a). In air, the $g_{d,\mu}$ asymmetry flipped: $g_{d,\mu}$ rose rapidly at a negative $V_G(V_{G3})$ and slowly at a positive $V_G(V_{G4})$ as shown in Fig. 2(b). This was attributed to the contact property change of the electrode and CNT (Ref. 3): at $V_G=0$, the Schottky barrier for holes ($\Phi_{bb}$) was high and that for electrons ($\Phi_{be}$) was low in vacuum [Fig. 2(c)], while $\Phi_{bb}$ was low and $\Phi_{be}$ was high in air [Fig. 2(d)]. Then $g_{d,\mu}$ rose slowly at $V_{G1}$, since the holes started to tunnel through a high $\Phi_{bb}$ [Fig. 2(e)], and $g_{d,\mu}$ rose rapidly at $V_{G2}$, since electrons started to tunnel through low $\Phi_{be}$ [Fig. 2(f)]. Similarly, $g_{d,\mu}$ rose rapidly at $V_{G3}$ because of low $\Phi_{bb}$ [Fig. 2(g)], and $g_{d,\mu}$ rose slowly at $V_{G4}$ because of high $\Phi_{be}$ [Fig. 2(h)]. In this $g_{d,\mu}$-$V_G$ experiment, the contact property modulation of the CNT in oxidation was much more influential than the bulk property change,8 and the experimental findings were consistently explained through the Schottky barrier modulation.

However, the standard Schottky (no pinning) theory9–12 does not explain this Schottky barrier modulation. In that theory, we must consider the system as a junction of an oxidized metallic electrode surface and a plain CNT or as a plain metallic electrode and an oxidized CNT, and align the bands at the contact. Usually, a gold surface is inert, thus insensitive to oxidation, so the first description is not appropriate. The second description turns out to give a qualitatively wrong result as discussed now. Generally, a negative charge at the material surface will increase the surface dipole...

FIG. 1. CNT FET with gate voltage $V_G$ in equilibrium ($V_D = 0$): (a) real-space charge distribution and (b) equivalent band structure along the arrow path above, where $A-D$ indicate corresponding points from (a).
and further confine the electrons within the material.\textsuperscript{8} Electron-negative oxygen molecules are negatively charged, so the CNT electron affinity $f_s$ in air should increase from $f_s$ in vacuum such that $f_s < f_s'$. Throughout this article, we use the convention that a prime indicates a quantity in air.

Figures 3(a)--3(d) represent band structures across the electrode-CNT junction. The CNT conduction- and valence-band edges are shown with the Fermi level $\zeta$, and $\chi_m$ is the work function of the metallic electrode. According to standard Schottky theory, we match the tops of $\chi_m$ and $f_s$ at the interface as shown in Figs. 3(a) and 3(b). Then $\Phi_{Bh}$ in vacuum and $\Phi_{Bh}'$ in air are expressed by

\begin{equation}
\Phi_{Bh} = E_G + f_s - \chi_m, \tag{1}
\end{equation}

\begin{equation}
\Phi_{Bh}' = E_G + f_s' - \chi_m. \tag{2}
\end{equation}

Thus $\Phi_{Bh} < \Phi_{Bh}'$, but this contradicts the experimental observations described above. In Schottky theory, all oxidation effects are represented in the modulated work function $f_s'$. It is clear that the Schottky theory does not explain the experiment consistently.

We will propose a model to overcome this difficulty and explain the Schottky barrier modulation consistently. Our model is related to the Bardeen theory regarding surface states.\textsuperscript{9-12} We will consider the electrostatic charge balance\textsuperscript{10} inside the Schottky junction, while this degree of freedom is not incorporated in the traditional concept of an "intimate Schottky junction" in Schottky theory. We will first demonstrate that our model certainly predicts a correct Schottky barrier modulation using energy band structures in Sec. II and then present a detailed mathematical formulation in Sec. III. The analytical solutions are given in the Appendix. The relevant equations are solved graphically to develop an intuitive understanding, and four different types of Schottky barrier modulations are discussed in Sec. IV. Experiments in Ref. 3 are examined using our model in Sec. V, and a summary is given in Sec. VI.

FIG. 2. CNT FET $g_{dV_G}$ characteristics and band structures with $V_D=0$: (a) $g_{dV_G}$ characteristics in vacuum, (b) $g_{dV_G}$ characteristics in air, (c) band structure in vacuum at $V_G=0$, (d) band structure in air at $V_G=0$, (e) band structure at $V_G$ in vacuum, (f) band structure at $V_G$ in vacuum, (g) band structure at $V_G$ in air, and (h) band structure at $V_G$ in air.

FIG. 3. Band structures for a Schottky junction between the metallic electrode and semiconducting CNT (a) in vacuum and (b) in air based on the conventional view of an intimate contact, resulting in the incorrect relation of low Schottky barrier for holes in vacuum $\Phi_{Bh}$ and high Schottky barrier for holes in air $\Phi_{Bh}'$; proposed band structures (c) in vacuum and (d) in air showing a potential drop $\Delta U'$ in the transition region, resulting in the correct relation of $\Phi_{Bh} < \Phi_{Bh}'$. Here $a$ is the transition region width, $\varepsilon_a$ is the dielectric constant, $f_s'$ is the CNT electron affinity, $\zeta$ is the CNT Fermi level, $\chi_m$ is the metallic work function, $\Phi_{Bh}$ is the hole Schottky barrier, and $\sigma_{ox}$ is the negative charge due to oxygen molecules.

FIG. 4. Schematic view of the transition region in the gold-electrode -- CNT interface, where gold clusters are formed and oxygen molecules are chemisorbed on top of the clusters.
II. SCHOTTKY BARRIER MODULATION MECHANISM

We consider here that the Schottky junction has a sandwich structure as shown in Fig. 4: a gold bulk electrode, gold clusters at the electrode surface, charged oxygen molecules, and the CNT surface. The region between the bulk electrode and CNT is called the “transition region.” In fact, a deposited gold surface has bumps with a width on the order of $10^{-1}$ $\mu$m (Ref. 13), and oxygen molecules can move into the gaps of the transition region (interface between electrode and CNT). Moreover, the electrode surface facing the CNT is expected to be microscopically flat, since during the electrode deposition process, gold atoms are attracted by the CNT (Ref. 14) and tend to form clusters. Although the microscopically flat gold surface is known to be inert to oxygen molecules, the clusters on the gold surface can chemisorb oxygen molecules at their tips and form $\text{O}_2^+$/$\text{Au}_{n}/\text{Au}(111)$ with an $n$-dependent binding energy ranging from $\sim 0.45$ to $-0.96$ eV ($n = 1–3$) (Ref. 15). These gold clusters have the highest occupied molecular orbitals (HOMO’s), and these orbitals are localized with their charge densities sticking out into the vacuum. Oxygen molecules bind to these sites. In each cluster, a charge transfer occurs from the gold HOMO to the oxygen $\pi^*$ orbital, and the oxygen molecule becomes negatively charged. The microscopically flat gold surfaces do not have these localized HOMO’s and are inert to oxygen molecules. Thus the presence of the CNT is critical for cluster formation and oxygen chemisorption on the gold electrode surface.

There are also discussions in the literature about interactions between oxygen molecules and the CNT. Some researchers have predicted physisorption of oxygen molecules on the CNT with negligible charge transfer, while others have predicted chemisorption of oxygen molecules on the CNT and estimated the transferred charge to be $\sim 0.1$ with a binding energy of $\sim 0.25$ eV (Ref. 17). In either case, the oxygen molecules dominantly interact with the gold surface clusters and are negatively charged by $-1$, regardless of whether the electrode and CNT are in an open- or closed-circuit condition.

The difference between the open- and closed-circuit conditions will appear in the distribution of the positive charge (which balances the oxygen’s negative charge). Under open-circuit conditions, the positive charge will appear mostly in the electrode, reflecting the dominant gold-oxygen interaction. However, under the closed-circuit conditions with $V_D = 0$, which is our case, the positive charge will move within the circuit and appear in both the electrode and CNT. This is how the system keeps the Fermi level constant everywhere. Once the circuit is closed, the distribution of the positive charge is determined by the electrostatics in the transition region, rather than the details of the oxygen-gold or oxygen-CNT interactions. We will study how the negative oxygen charge and resulting positive charge in the transition region modify the Schottky barrier under the closed-circuit condition.\(^{18}\)

The key conclusion is that the potential drop $\Delta U$ in the transition region is modified by oxidation. The negatively charged oxygen molecules will induce a balancing positive charge in the electrode and CNT, and $\Delta U$ will be modified. As will be shown in the following section, $|\Delta U|$ turns out to be small in vacuum and large in air. This will, in fact, lead to a correct Schottky barrier behavior consistent with the experiments in Ref. 3. We will show this with a $\mu$-CNT, but the same mechanism will also work for an $n$-CNT. For the two cases where $|\Delta U|$ is small in vacuum or large in air, the system has band structures as shown in Figs. 3(c) and 3(d), respectively. Thus we have $\Phi_{bh}$ in vacuum and $\Phi_{bh}$ in air:

\[
\Phi_{bh} = \phi_s + E_G - \chi_m - |\Delta U|, \quad (3)
\]

\[
\Phi_{bh} = \phi_s + E_G - \chi_m - |\Delta U'|. \quad (4)
\]

This time, $|\Delta U| < |\Delta U'|$ and $\Phi_{bh} > \Phi_{bh}'$, which is consistent with the experiments. $\chi_m$ is the work function for the plain metallic surface and $\phi_s$ is the electron affinity for the CNT. We use the free bulk material parameters $\phi_s$ and $\chi_m$ in Eqs. (3) and (4), and all oxidation effects are included in $\Delta U$.

The difference between the standard Schottky theory and our model is well represented in the band structures: $\Delta U$ is absent in the former as shown in Figs. 3(a) and 3(b), while $\Delta U$ is present and is significantly modified in oxidation in the latter as shown in Figs. 3(c) and 3(d). In the Schottky theory, $\Phi_{bh}$ is determined by the bulk properties only, through $\phi_s$ and $\chi_m$. In our model, $\Phi_{bh}$ is determined by the potential drop $\Delta U$ in the transition region reflecting the contact properties, in addition to the bulk properties $\phi_s$ and $\chi_m$. We will see in the next section that our model actually includes the standard Schottky theory as a special limit of vanishing transition layer width.

III. MATHEMATICAL FORMULATION

Now we will study how the potential drop $\Delta U$ is modulated in oxidation in our model. For this purpose, we will derive a relation for the CNT band bending $\phi_0$ and $\Delta U$ at a fixed $V_G$ based on the charge-neutrality relation\(^{10}\) within the planar junction theory\(^{5,12}\) under the closed-circuit condition. The negative oxygen charge $\sigma_{ox}$ per unit area is independent of the Fermi level $\zeta$ and is constant. There is a charge $\sigma_m$ per unit area on the metallic electrode surface and a charge $\sigma_{NT}$ per unit area within the CNT in the depletion or accumulation mode. The charge-neutrality relation requires

\[
\sigma_m + \sigma_{ox} + \sigma_{NT} = 0. \quad (5)
\]

That is, the positive countercharges $\sigma_m$ and $\sigma_{NT}$ must neutralize the negative $\sigma_{ox}$. Mathematically, this is equivalent to determining the CNT band bending $\phi_0$ for a given $\sigma_{ox}$. Then we would know how the positive charge divides between $\sigma_m$ and $\sigma_{NT}$. Analytical solutions of this problem are presented in the Appendix. Here we will provide graphical solutions to develop an intuitive understanding. The charge-neutrality condition can be split into two equations

\[
\sigma_c = -\sigma_m(\phi_0) = \Delta U \text{e}_v/\text{e}A = [\chi_m - (\phi_s + \phi_0 + \zeta)] \text{e}_v/\text{e}A, \quad (5a)
\]

\[
\sigma = \sigma_{NT}(\phi_0) + \sigma_{ox}, \quad (5b)
\]
where $e_u$ is an effective dielectric constant for the transition region (an appropriate average including the vacuum, gold clusters, and oxygen molecules, as discussed in Sec. V), $a$ is the width of the transition region, and $e$ is the unit charge. After specifying the system including the oxidation level, we know the functional forms of $\sigma = -\sigma_m(\phi_0)$ and $\sigma = \sigma_{NT}(\phi_0) + \sigma_{ox}$ for a given value of $\sigma_{ox}$. The intersection of these, Eqs. (5a) and (5b), defines $\phi_0$ and $\sigma$. Here $\sigma$ determines $\Delta U$ through Eq. (5a). Then we calculate $\Phi_{BB}$ by

$$\Phi_{BB} = \phi_o + E_G - \chi_m + \Delta U. \quad (6)$$

This is an extension of Eq. (3) and can be used for both positive and negative $\Delta U$. The gate voltage $V_G$ appears as a modulation of the Fermi level $\xi$ by

$$\xi = (V_G) = \xi_0 - aV_G. \quad (7)$$

where $\xi_0$ is a value at $V_G = 0$. In our definition, $\xi$ is measured from the bottom of the conduction band as in Figs. 3(c) and 3(d), rather than from the top of the valence band. A negative $V_G$ will increase the hole density and therefore increase $\xi$, while a positive $V_G$ will increase the electron density and therefore decrease $\xi$.

We will discuss the general shape of $\sigma = -\sigma_m(\phi_0)$ depending on whether the metallic work function $\chi_m$ is smaller or larger than the CNT work function $\phi_o + \xi$. When $\chi_m < \phi_o + \xi$, because of a shallow metallic work function $\chi_m$ or a large Fermi level $\xi$ at a large negative $V_G$, $\sigma = \sigma_{nt}(\phi_0)$ is as shown by the thick (largest $\xi \sim E_G$) or thin (large $\xi$) solid line with a negative slope, intersecting with the negative $\phi_0$ axis in Fig. 5(a). This is simply a standard charge-voltage relation for a capacitor. Only when $\chi_m = \phi_o + \phi_0 + \xi$ or the CNT band bending $\phi_0$ exactly compensates the work function difference $\chi_m - (\phi_o + \xi)$ do we have $\sigma = 0$. Otherwise, we have a finite $\sigma_m$ and therefore a finite $\Delta U$.

The same functional form of Eq. (5a) can be used for both $p$- and $n$-CNT's. When $\chi_m > \phi_o + \xi$, because of a deep metallic work function $\chi_m$ or a small Fermi level $\xi$ at a large positive $V_G$, $\sigma = \sigma_m(\phi_0)$ is as shown by the thin (small $\xi$) or thick (smallest $\xi \sim 0$) dashed line with a negative slope, intersecting with the positive $\phi_0$ axis in Fig. 5(a). If we change $V_G$ from negative to positive and modify the CNT from $p$ type to $n$ type, $\xi$ decreases monotonically from $-E_G$ to $0$, and $\sigma = -\sigma_m(\phi_0)$ will shift upward as the arrow indicates, from thick solid, to thin solid, to thin dashed, to thick dashed line.

Next, we will discuss the general shape of $\sigma = \sigma_{NT}(\phi_0) + \sigma_{ox}$ for $\sigma_{ox} = 0$. In fact, a finite negative $\sigma_{ox}$ simply shifts the entire curve downward, so the discussion can be limited to $\sigma_{ox} = 0$ without loss of generality. In the $p$-CNT case, accumulation occurs for $\phi_0 > 0$, and $\sigma = \sigma_{NT}(\phi_0)$ is positive and increases very rapidly with $\phi_0$. Depletion occurs for $\phi_0 < 0$, and $\sigma = \sigma_{NT}(\phi_0) = -(2e_{NT}\phi_0 N_B)^{1/2}$ is negative and has the shape of a parabola, based on planar junction theory, where $N_B$ is the effective CNT background (three-dimensional) charge density determined by $\xi$ and therefore by $V_G$ through Eq. (7). Thus $\sigma = \sigma_{NT}(\phi_0)$ for $p$-CNT follows the thick (largest $\xi \sim E_G$, large $N_B$) or thin (large, $\xi$, small $N_B$) solid curve in Fig. 5(b). In the $n$-CNT case, accumulation occurs for $\phi_0 < 0$, and $\sigma = \sigma_{NT}(\phi_0)$ is negative and decreases very rapidly with decreasing $\phi_0$. Depletion occurs for $\phi_0 > 0$, and $\sigma = \sigma_{NT}(\phi_0) = -(2e_{NT}\phi_0 N_B)^{1/2}$ is positive and has the shape of a parabola. Thus $\sigma = \sigma_{NT}(\phi_0)$ for $n$-CNT follows the thin (small, $\xi$, small $N_B$) or thick (smallest $\xi \sim 0$, large $N_B$) dashed curve in Fig. 5(b). If we change $V_G$ from negative to positive and modify the CNT from $p$ type to $n$ type, $\xi$ decreases monotonically from $-E_G$ to $0$. Thus the curve will change as the arrow indicates, from thick solid, to thin solid, to thin dashed, to thick dashed curve. When $\xi \sim E_G/2$ and the CNT is almost intrinsic, the curve approaches the horizontal axis $\sigma = 0$, since the band bending $\phi_0$ does not produce any appreciable charge $\sigma$ in the CNT. Inversion will occur for large $|\phi_0|$, but the intersections of interest in this case occur in the accumulation and depletion portions. The inversion onsets are not shown in the figure.

In the standard Schottky theory, the relation $\chi_m = \phi_o + \phi_0 + \xi$ is assumed a priori. Mathematically, our model includes standard Schottky theory as a special limiting case of vanishing transition region width $a \rightarrow 0$. Then $V_G = e/a \rightarrow \infty$ and the relation $\chi_m = \phi_o + \phi_0 + \xi$ must hold to avoid the divergence on the right-hand side of Eq. (5a). Physically, this means that the CNT band bending $\phi_0$ exactly compensates the work function difference $\chi_m - (\phi_o + \xi)$ when $a \rightarrow 0$. In this limit, to achieve electrostatic balance within the Schottky junction by neutralizing the oxygen molecule charge $\sigma_{ox}$, a degree of freedom is removed from our model, and $\phi_0$ is determined only by the properties of the bulk farther away from the junction. The right-hand side of Eq. (5a) has the form of $0 \times \infty$ and the metallic charge $\sigma_m$ is uncertain. Graphically, the solution of Eq. (5a) is almost vertical, and the intersection of Eqs. (5a) and (5b) is uncertain, or its location can be anywhere on the $\sigma$ axis. This uncertainty leaves room for the concept of modified bulk parameters in oxidation, but as we have already seen with a band structure scheme, this approach is physically inappropriate and will lead to contradictory results. The explicit inclusion of a finite $\sigma_{ox}$ in the transition region with a finite $a$ as we have done in our model is essential in explaining the experimental observations.

**IV. FOUR SCHOTTKY BARRIER MODULATIONS**

Depending on whether the CNT is $p$ type or $n$ type and on whether the metallic work function $\chi_m$ is smaller or larger...
than the CNT work function $\phi_0 + \xi$, there are four different cases, as illustrated in Fig. 6.

(i) $p$-CNT when $\chi_m > \phi_0 + \xi$ (line “$\gamma$”). In vacuum, $\sigma = \sigma_{NT}(\phi_0) + \sigma_{ox}$ with $\sigma_{ox} = 0$ is curve “$\alpha_0$” in Fig. 6(a), and the intersection with line “$\gamma$” is $A0$. Here $A0$ has a large negative (downward) band bending $\phi_0$ in the depletion mode and a small negative $\sigma$ corresponding to a small negative (right up, left down) $\Delta U$ from Eq. (5). The band structure at $A0$ is shown in Fig. 6(c). As the oxidation progresses, $\sigma_{ox}$ becomes more and more negative. $\sigma = \sigma_{NT}(\phi_0) + \sigma_{ox}$ shifts downward and forms curves “$\alpha_1$” and “$\alpha_2$,” and the intersection with line “$\gamma$” moves down as $A0 \rightarrow A1 \rightarrow A2$. In the weak oxidation (“$\alpha_1$”) of $0 > \sigma_{ox} > [\chi_m - (\phi_0 + \xi)]e_u/ea$, A1 has a small negative $\phi_0$ in the depletion mode and a large negative $\sigma$ corresponding to a large negative $\Delta U$. In the strong oxidation (“$\alpha_2$”) of $[\chi_m - (\phi_0 + \xi)]e_u/ea > \sigma_{ox}$, A2 has a negligible $\phi_0 \sim 0^+$ (almost flatband) in the accumulation mode and the largest negative $\sigma$ corresponding to the largest negative $\Delta U$. The band structure at A2 is shown in Fig. 6(d). It is clear that $\Phi_{bh}$ decreases appreciably in oxidation. Physically, a negative oxygen charge $\sigma_{ox}$ reduces the negative dopant charge in the p-CNT to satisfy the charge-neutrality condition, leading to an appreciable band bending reduction. Once the oxidation reaches $\sigma_{ox} = [\chi_m - (\phi_0 + \xi)]e_u/ea > \sigma_{ox}$, no further significant Schottky barrier modulation is expected.

(ii) $p$-CNT when $\chi_m > \phi_0 + \xi$ (line “$\eta$”). Line “$\eta$” intersects only at the accumulation portion of $\sigma = \sigma_{NT}(\phi_0) + \sigma_{ox}$, regardless of the value of $\sigma_{ox}$, as shown in Fig. 6(a). All intersections are of the $Bcf$ type, in the first quadrant. The $Bcf$ condition has a negligible $\phi_0 \sim 0^+$ and a large positive $\sigma$ corresponding to a large positive $\Delta U$. The band structure at $Bcf$ is shown in Fig. 6(e). The $p$-CNT is consistently in the accumulation mode. Thus there is negligible change in $\phi_0$ and $\Delta U$, and the oxidation will not modify $\Phi_{bh}$ practically. Physically, the metallic work function is so deep that the electronic charge must be negative and the CNT charge must be positive. The p-CNT is therefore locked into the accumulation mode and provides a positive charge. A negative oxygen charge $\sigma_{ox}$ increases the already ample positive accumulation charge in the p-CNT to satisfy the charge-neutrality condition, but this is done without a practical change in the band bending. The Schottky barrier modulation is negligible.

(iii) $n$-CNT when $\chi_m > \phi_0 + \xi$ (line “$\eta$”). In vacuum, $\sigma = \sigma_{NT}(\phi_0) + \sigma_{ox}$ with $\sigma_{ox} = 0$ is shown by curve “$\beta_0$” in Fig. 6(b), and the intersection with line “$\eta$” is $B0$. Here $B0$ has a small positive $\phi_0$ in the depletion mode and a small positive $\sigma$ corresponding to a small positive $\Delta U$. The band structure at $B0$ is shown in Fig. 6(f). As the oxidation progresses, $\sigma = \sigma_{NT}(\phi_0) + \sigma_{ox}$ shifts downward and forms curves “$\beta_1$” and “$\beta_2$,” and the intersection with line “$\eta$”

FIG. 6. Graphical solution of our model by finding the intersections of a metallic electrode charge line “$\gamma$” or “$\eta$” and a charge curve “$\alpha_i$” or “$\beta_i$” $(i = 0, 1, 2$) for the CNT and oxygen molecules as a function of band bending $\phi_0$. Here “$\gamma$” is for $\chi_m < \phi_0 + \xi$, and “$\eta$” is for $\chi_m > \phi_0 + \xi$, where $\chi_m$ is the metallic electrode work function, $\phi_0$ is the CNT electron affinity, and $\xi$ is the Fermi level. (a) is for the p-CNT case and (b) is for the n-CNT case. $i = 0$ corresponds to vacuum (oxygen charge $\sigma_{ox} = 0$), $i = 1$ to weak oxidation (small negative $\sigma_{ox}$), and $i = 2$ to strong oxidation (large negative $\sigma_{ox}$). Band structures are shown for the resulting operating points: (c) $A0$ for a p-CNT in vacuum and (d) $A2$ for a p-CNT in air, demonstrating the correct relation $\Phi_{bh} > \Phi'_{bh}$; (e) $Bcf$ for a p-CNT in vacuum with extremely deep $\chi_m$; (f) $B0$ for an n-CNT in vacuum and (g) $B1$ for an n-CNT in air, demonstrating the correct relation $\Phi_{be} < \Phi'_{be}$; (h) $Acf$ for an n-CNT in vacuum with an extremely shallow $\chi_m$. 

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moves downward as \( B0 \rightarrow B1 \rightarrow B2 \). The \( n \)-CNT is locked into the depletion mode regardless of the value of \( \sigma_{\alpha} \). Here \( B2 \) in the strong oxidation has a large positive \( \phi_0 \) and a large negative \( \sigma \) corresponding to a large negative \( \Delta U \). The band structure at \( B2 \) is shown in Fig. 6(b). It is clear that \( \Phi_{Be} \) increases appreciably in oxidation. Physically, a negative oxygen charge \( \sigma_{\alpha} \) requires more positive dopant charge in the \( n \)-CNT to satisfy the charge-neutrality condition, and this results in a further large positive band bending. The Schottky barrier modulation is significant.

(iv) \( n \)-CNT when \( \chi_m < \phi_0 + \xi \) (line ”\( \gamma \)”). In vacuum, the intersection with line ”\( \gamma \)” occurs at the \( n \)-CNT accumulation portion of \( \sigma = \sigma_{\alpha}(\phi_0) + \sigma_{\alpha} \), which corresponds to the \( Acf \) region in Fig. 6(b). In weak oxidation where \( 0 > \sigma_{\alpha} > [\chi_m - (\phi_0 + \xi)]e_u/e_a \), the intersection with line ”\( \gamma \)” occurs at the accumulation portion consistently. The \( Acf \) condition has a negligible band bending \( \phi_0 \sim 0 \) and a large negative \( \sigma \) corresponding to a large negative \( \Delta U \). The band structure for the \( Acf \) condition is shown in Fig. 6(h). The band bending does not change substantially, and \( \Phi_{Be} \) modulation is negligible. In strong oxidation where \( [\chi_m - (\phi_0 + \xi)]e_u/e_a > \sigma_{\alpha} \), the \( n \)-CNT is in the depletion mode, and a finite positive \( \phi_0 \) and a large negative \( \sigma \) are expected, leading to a finite increase in \( \Phi_{Be} \). Physically, the metallic work function is so shallow that the electrode charge must be positive and the \( n \)-CNT charge must be negative. A negative-charge \( \sigma_{\alpha} \) requires a decrease in the negative charge in the positive- \( V_G \) to satisfy the charge-neutrality condition, and this requirement is met by reducing the \( n \)-CNT accumulation charge until \( \sigma_{\alpha} = [\chi_m - (\phi_0 + \xi)]e_u/e_a \). Once \( \sigma_{\alpha} \) exceeds this limit, the \( n \)-CNT cannot reduce the accumulation charge further. The \( n \)-CNT must provide a positive charge, which is possible in the depletion mode. Thus a finite positive \( \phi_0 \) results, and there is a finite Schottky barrier modulation. Therefore, in the weak-oxidation case of \( 0 > \sigma_{\alpha} > [\chi_m - (\phi_0 + \xi)]e_u/e_a \), the Schottky barrier modulation is negligible, but in the strong-oxidation case of \( [\chi_m - (\phi_0 + \xi)]e_u/e_a > \sigma_{\alpha} \), a finite Schottky barrier modulation is expected.

V. DISCUSSION

As we have seen in Fig. 2, the Schottky barrier modulation due to oxidation was significant for both negative- and positive- \( V_G \)-bias conditions in Ref. 3. Thus we can exclude cases (ii) and (iv). The CNT was \( p \)-type at the negative- \( V_G \) onset at \( V_{G1} \) in vacuum and at \( V_{G3} \) in air, and this should correspond to case (i). Then the condition \( \chi_m < \phi_0 + \xi \) had to be satisfied. Similarly, the CNT was \( n \)-type at the positive- \( V_G \) onset at \( V_{G2} \) in vacuum and at \( V_{G4} \) in air, and this should correspond to case (iii). Then the condition \( \chi_m > \phi_0 + \xi \) had to be satisfied. Therefore, we had \( \chi_m < \phi_0 + \xi \) for a negative \( V_G \) and \( \chi_m > \phi_0 + \xi \) for a positive \( V_G \), or in other words, \( V_G \) was the major mechanism to determine the sign of \( \chi_m - (\phi_0 + \xi) \). This is possible when the work function difference at \( V_G = 0 \), \( [\chi_m - (\phi_0 + \xi)]_0 \), was small enough compared to the band gap \( E_G \) in the gold-CNT system. We believe that this was in fact the case and can now assign a band structure including the electrostatic balance in the transition region for each \( V_{Gi} \) onset (\( i = 1 \sim 4 \)) in Fig. 2: Figure 6(c) corresponds to \( V_{G1} \), Fig. 6(f) corresponds to \( V_{G2} \), Fig. 6(d) corresponds to \( V_{G3} \), and Fig. 6(g) corresponds to \( V_{G4} \). Because of an obvious relation \( \Phi_{Be} = \Phi_{Be} + \Phi_{Be} = E_G \), a large positive band bending \( \phi_0 \) at \( V_{G1} \) should occur with a small negative band bending \( \phi_0 \) at \( V_{G2} \) in vacuum. In air, a small negative band bending \( \phi_0 \) at \( V_{G3} \) should occur with a large positive band bending \( \phi_0 \) at \( V_{G4} \). We can clearly see this trend. The experimentally observed Schottky barrier modulation is consistently explained qualitatively.

We next estimate the relevant numerical values. In order to define the negative oxygen charge density, we project the charged oxygen molecules from the rough surface onto a planar gold (111) surface. If \( \Gamma_{ox} \% \) of the gold plane is covered with oxygen molecules, corresponding to \( \Gamma_{ox} \) oxygen molecules per 100 gold atoms, \( \sigma_{\alpha} = -1.86 \times 10^{14} \Gamma_{ox} \text{cm}^{-2} \). Then the contribution of \( \sigma_{\alpha} \) to \( \Delta U \) is estimated to be 0.251a (\( \AA \)) \( \Gamma_{ox} \% \text{e}/e_v \text{V} \). According to an adsorption experiment of the gold free cluster-oxygen molecule system at room temperature, the reaction completion ratio is quite high, larger than 80% (Ref. 19). We can expect a similarly high completion ratio for the supported clusters in vacuum, the Au(111) surface facing the CNT, which is the case of interest. It has to be emphasized that \( \Gamma_{ox} \) is literally the oxygen chemisorption coverage density, but is more directly related to the gold cluster density, given that the reaction completion ratio is high. The gold cluster height \( b \) with an attached oxygen molecule is 2–4 \( \AA \) (Ref. 15). Thus we expect the transition region width to be \( a \sim 3–5 \text{ Å} \). Generally, gases, including oxygen, have a dielectric constant close to unity.2 The gold clusters effectively increase the dielectric constant by \( 1/[1 – b/a] \) multiplied by an appropriate weighting factor (a function of \( \Gamma_{ox} \)), reflecting the partial coverage with clusters.22 Thus we expect \( \epsilon_{\alpha} \sim 10^{4} \). Given \( a \sim 3–5 \text{ Å} \) and \( \epsilon_{\alpha} \sim 10^{3} \), we find that the projected oxygen density \( \Gamma_{ox} \) needs to be at least \( (1 \times 10^{-1} \times 10^{0}) \% \) for \( a \Gamma_{ox} e_v \) to be on the order of unity. Then the contribution of \( \sigma_{\alpha} \) to \( \Delta U \) is a few tenths of an electronvolt, which is comparable to a CNT band gap \( E_G \sim 0.5 \text{ eV} \) for an example semiconducting (17,0) CNT (Ref. 23), and our present model describes the Schottky barrier modulation appropriately. The projected oxygen density \( \Gamma_{ox} \) or the gold cluster density can be estimated experimentally to test our model.

Case (ii) will occur for an extremely deep metallic work function \( \chi_m \) as shown in Fig. 6(e). Case (iv) will occur for an extremely shallow metallic work function as shown in Fig. 6(h). In either case, the CNT is locked into the accumulation mode in vacuum, and there is little Schottky barrier modulation. Recently, Ref. 8 has reported CNT FET’s with a pre-threshold slope approaching that of a silicon metal-oxide-semiconductor (MOS) FET. The contacts of these CNT FET’s are practically Ohmic and are considered to be related to these extreme work function limits.

The Schottky barrier can be modulated if we introduce a charge at the interface between the electrode and CNT. The charge does not have to originate from gas molecules, but can be from any source. A negative charge will lower the
Schottky barrier for holes, and a positive charge will lower the Schottky barrier for electrons. Thus we need a negative charge for \( p \)-CNT and a positive charge for \( n \)-CNT to create a good Ohmic contact. By choosing electrode metals carefully, we can achieve either case (ii) or (iv). These cases would be preferable in electronics applications, since the contact properties are insensitive to oxidation (more stable), and an Ohmic contact is quite possible in these limits.

VI. SUMMARY

We have presented a model for Schottky barrier modulation under oxidation in the electrode-CNT system. The model considers an appreciable potential drop change in the transition region due to negatively charged oxygen molecules, in contrast to the standard Schottky theory, which does not consider this degree of freedom at all. The gold surface facing the CNT will have clusters, and oxygen molecules are chemisorbed on top of these clusters. Oxidation increases this potential drop and therefore modifies the Schottky barrier. We have explained how high \( \Phi_{Bh} \) in vacuum and low \( N_B \) in air are possible by showing the behavior of the band structures. The electrode, the transition region with negatively charged oxygen molecules, and the CNT are treated equally in our model. The negatively charged oxygen molecules induce a counterbalancing positive charge in both the electrode and CNT. How this charge is divided between \( \sigma_m \) and \( \sigma_\text{NT} \) is determined by the electrostatics in the transition region. In the gold-CNT system in Ref. 3, the work function difference between the electrode and CNT had to be small, and Schottky barrier modulation was possible for both holes and electrons. Schottky barrier modulation is large when a CNT depletion mode is involved, while modulation is negligible when a CNT accumulation mode is involved. The negative-charge density \( \sigma_\text{ox} \) corresponding to a coverage of 0.1\%-1\% of the gold surface is enough to observe the expected Schottky barrier modulation. Finally, we showed that a Schottky barrier can be modulated by intentionally introducing a charge in the transition region, which approach may be useful in achieving a good Ohmic contact.

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APPENDIX: ANALYTICAL SOLUTIONS

If we apply a gate voltage \( V_G \), carriers are induced in the CNT. Then the CNT Fermi level \( \zeta = \zeta (V_G) \) and the effective background doping \( N_B = N_B (V_G) \) are determined. The electron affinity for a free CNT is \( \phi_s \). By specifying the electrode material, we know the work function \( \chi_m \) for a free surface. The transition region width \( a \) and its dielectric constant \( \varepsilon_s \) can be determined either theoretically or empirically. Using these quantities, we will express the CNT band bending as \( \phi_0 \) and the potential drop in the transition region as \( \Delta U \). Two positive energies \( U_\text{ox} \) and \( U_B \) and the dielectric constant ratio \( \kappa \) are defined by

\[
U_\text{ox} = e a \sigma_\text{ox} / \varepsilon_s ,
\]

\[
U_B = e^2 N_B a^2 / 2 \varepsilon_\text{NT} ,
\]

\[
\kappa = \varepsilon_\text{NT} / \varepsilon_s ,
\]

where \( \varepsilon_\text{NT} \) is the CNT dielectric constant and \( \sigma_\text{ox} \) is the oxygen density. The \( p \)-CNT and \( n \)-CNT scenarios are discussed separately.

(i) \( p \)-CNT scenario. When \(- \chi_m + \phi_s + \zeta \leq U_\text{ox} \) (accumulation, \( \phi_0 > 0 \)), an ample accumulation charge is available without noticeable band bending. Thus the solution is given by

\[
\phi_0 \sim 0^+ .
\]

When \(- \chi_m + \phi_s + \zeta \geq U_\text{ox} \) (depletion, \( \phi_0 < 0 \)), Eq. (5) in Sec. III is modified to Eq. (A3) and its solution is given in Eq. (A4) by

\[
( - \phi_0 ) + 2 \kappa ( U_B \phi_0 )^{1/2} + \chi_m - \phi_s - \zeta + U_\text{ox} = 0 , \tag{A3}
\]

\[
\phi_0^{1/2} = [ - U_B^{1/2} + ( U_B - \chi_m + \phi_s + \zeta - U_\text{ox} )^{1/2} ] / \kappa . \tag{A4}
\]

(ii) \( n \)-CNT scenario. When \(- \chi_m + \phi_s + \zeta \leq U_\text{ox} \) (accumulation, \( \phi_0 < 0 \)), an ample accumulation charge is available without noticeable band bending. Thus the solution is given by

\[
\phi_0 \sim 0^- .
\]

When \(- \chi_m + \phi_s + \zeta \geq U_\text{ox} \) (depletion, \( \phi_0 > 0 \)), Eq. (5) is modified to Eq. (A6) and its solution is given in Eq. (A7) by

\[
\phi_0 + 2 \kappa ( U_B \phi_0 )^{1/2} - \chi_m + \phi_s + \zeta - U_\text{ox} = 0 , \tag{A6}
\]

\[
\phi_0^{1/2} = [ - U_B^{1/2} + ( U_B + \chi_m - \phi_s - \zeta + U_\text{ox} )^{1/2} ] / \kappa . \tag{A7}
\]

In both scenarios, once \( \phi_0 \) is obtained, \( \Delta U \) is evaluated by

\[
\Delta U ( \phi_0 ) = \chi_m - ( \phi_s + \phi_0 + \zeta ) , \tag{A8}
\]

and then the Schottky barrier \( \Phi_{Bh} \) is given by

\[
\Phi_{Bh} = \phi_s + E_G - \chi_m + \Delta U ( \phi_0 ) . \tag{A9}
\]

When \( \sigma_\text{ox} = 0 \), the familiar boundary condition for electric flux density continuity is satisfied at the interface of the transition region and CNT. In fact, using Eq. (A8), we have
where Eqs. (A3) or (A6), with $U_{\alpha}=0$, is used at the second equality. The derivative of $\phi_0$ along the depletion layer length $l$ is related to $\sigma_{\text{NT}}(\phi_0)$ and is given with the planar junction theory^5 by

$$e_{NT}|d\phi_0/dl| = e|\sigma_{\text{NT}}(\phi_0)| = e(2\varepsilon_{\text{NT}}|\phi_0|N_B)^{1/2},$$

(A11)

Thus $e_{\alpha}|\Delta U/l|$ in the transition region and $e_{\text{NT}}|d\phi_0/dl|$ in the CNT are the same and the electric flux density is certainly continuous at the interface.

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7 We consider a series connection of an oxide capacitance $C_\alpha$ and a CNT capacitance $C_{\text{CNT}}$ between the doped substrate and grounded electrode, and $\sigma_a = C_\alpha/[C_\alpha+C_{\text{CNT}}]$.

8 In recent CNT FET experiments by A. Javey, H.-S. Kim, M. Brink, Q. Wang, A. Ural, J. Guo, P. McIntyre, P. McEuen, M. Lundstrom, and H. Dai, Nature Mat. 1, 241 (2002); A. Javey, J. Guo, M. Lundstrom, and H. Dai, Nature (London) 424, 654 (2003), the Ohmic contact was achieved by practically eliminating the Schottky barrier through an appropriate choice of electrode material and the adoption of chemical processing for the contact with an optimized transistor geometry.


12 F. Leonard and J. Tersoff, Phys. Rev. Lett. 84, 4693 (2000), end and side contacts are compared in placing an electrode on a semiconducting CNT. Unique properties are expected in the end contact case, while traditional properties are expected in the side contact case. Here we deal with the latter as shown in Fig. 1, and