Modeling of Schottky barrier modulation due to oxidation at metallic electrode and semiconducting carbon nanotube junction

Toshishige Yamada\textsuperscript{a)}

NASA Ames Research Center, M/S 229-1, Moffett Field, California, 94035-1000

A model is proposed for the previously reported lower Schottky barrier for holes $\Phi_{Bh}$ in air than in vacuum at a metallic electrode – semiconducting carbon nanotube (CNT) junction. We assume that there is a transition region between the electrode and the CNT, and an appreciable potential can drop there. The role of the oxidation is to increase this potential drop with negatively charged oxygen molecules on the CNT, leading to lower $\Phi_{Bh}$ after oxidation. The mechanism prevails in both $p$- and $n$-CNTs, and the model consistently explains the key experimental findings.
In air, a carbon nanotube (CNT) is oxidized and oxygen molecules stay at the CNT surface. The IBM group built CNT field-effect transistors (FETs) [1] and measured the channel conductance \( g_d \) as a function of gate voltage \( V_G \). They concluded that the Schottky barrier \( \Phi_B \) between the metallic electrode and the semiconducting CNT at the source or drain contact was modulated in oxidation [2]. In vacuum, \( g_d \) rose slowly at \( V_{G1} < 0 \) and rapidly at \( V_{G2} > 0 \) in Fig. 1(a) because \( \Phi_B \) for holes (\( \Phi_{Bh} \)) was high and \( \Phi_B \) for electrons (\( \Phi_{Be} \)) was low as in the band structures at \( V_{G1} \) and \( V_{G2} \) in Figs. 1(b) and 1(c), respectively, where the CNT conduction and valence edges are shown and \( \alpha \) is a device constant [3]. In air, the \( g_d \) asymmetry flipped in Fig. 1(d) because \( \Phi_{Bh} \) was low and \( \Phi_{Be} \) was high due to oxidation as in the band structures at \( V_{G3} \) and \( V_{G4} \) in Figs. 1(e) and 1(f), respectively. If the main role of oxidation had been to dope the bulk CNT \( p \)-type rather than to modify \( \Phi_B \), the entire \( g_d-V_G \) characteristics would have simply shifted horizontally without the \( g_d \) asymmetry flip. This is the basis of the \( \Phi_B \) modulation in oxidation.

In this letter, we propose a model and explain how \( \Phi_{Bh} \) can decrease in oxidation. The oxidation seems to result in the opposite, i.e., an increase in \( \Phi_{Bh} \) at first glance. In fact, oxygen molecules are expected to be negatively charged on the CNT because of the large electronegativity. The negative charge may not necessarily come only from the CNT, but also from the environment [4]. Generally, negative charge at the material surface will increase the surface dipole providing the confinement mechanism for electrons within the material bulk [4]. Thus, the CNT electron affinity \( \phi_s \) should increase in oxidation such that \( \phi_s < \phi_{s'} \), where a quantity in vacuum is denoted without a prime and that in air is denoted with a prime. According to the standard band-alignment theory at the interface [5], \( \Phi_{Bh} \) is determined with the electron work function \( \chi_m \) of the metallic electrode and \( \phi_s \) by \( \Phi_{Bh} = E_G + \phi_s - \chi_m \) as in Fig. 2(a), where the CNT conduction and valence edges are shown with the band gap \( E_G \) and the Fermi energy \( \zeta \). The influence of oxidation appears
only in \( \phi_s \), and we will have \( \Phi_{Bh} < \Phi_{Bh}' \) and \( \Phi_{Be} = E_G - \Phi_{Bh} > \Phi_{Be}' = E_G - \Phi_{Bh}' \) in Fig. 2(b) after oxidation, but these relations are contradictory to the experimental results [2].

This view is defective in two ways. (1) It assumes that the metallic electrode – semiconducting CNT junction is so abrupt that there is no transition region between the electrode and the CNT and there is no appreciable potential drop there. However, this may not be the case. (2) Indeed \( \phi_s \) will increase in oxidation and become \( \phi_s' (> \phi_s) \) on a free CNT surface [6]. However, in the junction structure consisting of the electrode and the CNT, it is not certain whether the oxidation effect can be represented as the electronic property modulation in the CNT side only [7]. A cruder way to say this is that the work functions of the electrode and the CNT should be both modified in oxidation, but from the beginning, the separate work functions will not have meaning in the junction structure.

Our model overcomes these difficulties. We assume a transition region between the electrode and the CNT, where an appreciable potential \( \Delta U \) can drop. We will argue that \( \Delta U \) is modified in oxidation, and this explains the \( \Phi_B \) difference in vacuum and in air [2], by taking an example of a p-CNT for illustration, but the same mechanism will also work for an n-CNT. In vacuum in Fig. 2(c), \( \Delta U \) is small. The p-CNT depletes near the junction interface, and the depletion region provides negative charge. This negative charge is neutralized by the positive charge on the CNT and the other positive charge on the electrode. In air in Fig. 2(d), \( \Delta U' \) is large, since the oxygen is negatively charged at the CNT surface and raises the potential at the interface. This negative charge is neutralized by the positive charge in the CNT and the other positive charge on the electrode. In this picture, we have \( \Phi_{Bh} = \phi_s + E_G - \chi_{th} - \Delta U \). The effect of oxidation appears only in \( \Delta U \), and \( \Delta U \) in vacuum is smaller than \( \Delta U' \) in air. Therefore, \( \Phi_{Bh} > \Phi_{Bh}' \) and accordingly \( \Phi_{Be} < \Phi_{Be}' \), which are the correct relations consistent with the experiments [2].
The role of $V_G$ in a CNT FET is to change the channel doping effectively. With the application of $V_G$, positive and negative charges are introduced as in Fig. 3(a). The electric field is mostly vertical, and the horizontal component is negligible due to the extremely thin geometry of the CNT. If we consider a band structure along the arrow path from the metallic source, through the CNT, to the metallic drain, the band bending occurs only in the depletion regions below the source and the drain since the path is parallel to the electric field only there. Thus, the energy band structure with the CNT conduction and valence edges will have a shape in Fig. 3(b), where A-D indicate corresponding points on the path. The negative charge density in the depletion region in the band picture has to be consistent with the induced carrier density in the CNT channel. Thus, the effect of $V_G$ can be absorbed in the redefinition of $\zeta$ and the effective background doping density $N_B$. The charge neutrality relation holds for both the original and the equivalent band pictures.

We will derive a relation for the CNT band bending $\phi_0$ and $\Delta U$ based on this charge neutrality relation, assuming that the oxygen molecules are negatively charged and physisorbed to the CNT, so that their charge $\sigma_{ox}$ is constant, independent of $\phi_0$ and $\zeta$. There are charge $\sigma_m$ on the metallic electrode and charge $\sigma_{NT}$ within the CNT in the depletion or accumulation mode. The neutrality relation requires $\sigma_m + \sigma_{ox} + \sigma_{NT} = 0$, and this determines $\Delta U$ as a function of $\phi_0$. Before discussing analytical solutions, we will find solutions graphically through the intersection of two graphs

$$\sigma = -\sigma_m(\phi_0) = [\chi_m - (\phi_s + \phi_0 + \zeta)]e_0/e and \sigma = \sigma_{NT}(\phi_0) + \sigma_{ox},$$

where $\varepsilon_{tr}$ is a dielectric constant, $a$ is a width of the transition region, and $e$ is the unit charge. The intersection defines $\phi_0$ and $\Delta U = e\sigma_m(\phi_0)/C_G$. Then, we calculate $\Phi_{Bh} = \phi_s + E_G \cdot \chi_m - \Delta U$ and $\Phi_{Be} = \chi_m + \Delta U - \phi_s$.

$\sigma = -\sigma_m(\phi_0)$ is a straight line like "ka" with a negative slope. It depends on the CNT only through $\zeta$, and its functional form is the same for $p$- and $n$-CNTs. $\sigma = \sigma_{NT}(\phi_0) + \sigma_{ox}$ is different for $p$- and $n$-CNTs as in Figs 4(a) and 4(b), and we will examine these scenarios separately. In the
$p$-CNT scenario, accumulation occurs for $\phi_0 > 0$ and positive $\sigma_{NT}(\phi_0)$ increases rapidly with $\phi_0$, while inversion occurs for $\phi_0 < 0$ and negative $\sigma_{NT}(\phi_0) = -(2\varepsilon_{NT}\phi_0 N_B)^{1/2}$ is a horizontal parabola with the planar junction theory [5]. In vacuum, $\sigma_{ox} = 0$ and $\sigma_{NT}(\phi_0)$ is line "$\alpha 0$" in Fig. 4(a). As the oxidation progresses and $\sigma_{ox}$ becomes more negative, $\sigma_{NT}(\phi_0) + \sigma_{ox}$ shifts downward and forms lines "$\alpha 1$" and "$\alpha 2$". Thus, the intersection moves down from A0 through A1 to A2. This means that the band bending is large downward $\phi_{0A0} < 0$ in vacuum at A0 in Fig. 4(c), but becomes flatter with the oxidation. In the heavy oxidation limit at A2, the CNT is in the accumulation mode and the band bending is slightly upward $\phi_{0A2} > 0$ in Fig. 4(d). It is clearly seen that $\Phi_B$ decreases appreciably in oxidation when $\gamma_m - \phi_s - \zeta \leq 0$, corresponding to line "$ka$". Otherwise, the CNT is consistently in the accumulation mode, resulting in very little change in $\phi_0$ as is the case for line "$kb$". In the $n$-CNT scenario, accumulation occurs for $\phi_0 < 0$ and negative $\sigma_{NT}(\phi_0)$ decreases very rapidly with decreasing $\phi_0$, while inversion occurs for $\phi_0 > 0$ and positive $\sigma_{NT}(\phi_0) = +(2\varepsilon_{NT}\phi_0 N_B)^{1/2}$ is a horizontal parabola. In vacuum, $\sigma_{ox} = 0$ and $\sigma_{NT}(\phi_0)$ is line "$\beta 0$" in Fig. 4(b). As the oxidation progresses, $\sigma_{NT}(\phi_0) + \sigma_{ox}$ shifts downward and forms lines "$\beta 1$" and "$\beta 2$", and the intersection moves again downward from B0 through B1 to B2. The band structures at B0 with $\phi_{0B0} < 0$ and B1 with $\phi_{0B1} < 0$ are shown in Figs. 4(e) and 4(f), respectively. Unlike the $p$-CNT case, we should expect a significant change in $\phi_0$ and therefore a significant $\Phi_B$ modulation for various values of $\gamma_m - \phi_s - \zeta$, for "$ka$" and "$kb$".

We will give analytical solutions by defining two positive energies, $U_B = e^2 N_B a^2 / 2 \varepsilon_{tr}$ and $U_{OX} = e a \sigma_{ox} / \varepsilon_{tr}$. In the $p$-CNT scenario, accumulation ($\phi_0 > 0$) occurs for $- \gamma_m + \phi_s + \zeta \leq U_{OX}$ and we can approximate $\phi_0 \sim 0$. Inversion ($\phi_0 < 0$) occurs for $- \gamma_m + \phi_s + \zeta \leq U_{OX}$ and $(-\phi_0)^{1/2}$ satisfies a quadratic equation $(-\phi_0) + 2(U_B |\phi_0|)^{1/2} + \gamma_m - \phi_s - \zeta + U_{OX} = 0$. Its solution is $(-\phi_0)^{1/2} = - (U_B)^{1/2} + (U_B - \gamma_m + \phi_s + \zeta - U_{OX})^{1/2}$. In the $n$-CNT scenario, accumulation ($\phi_0 < 0$) occurs for $- \gamma_m + \phi_s +$
\[ \zeta \geq U_{OX} \] and we can approximate \( \phi_0 \sim 0 \). Inversion (\( \phi_0 > 0 \)) occurs for \( -\chi_m + \phi_s + \zeta \leq U_{OX} \), and \( \phi_0^{1/2} \) satisfies an equation \( \phi_0 + 2(U_B\phi_0)^{1/2} - \chi_m + \phi_s + \zeta - U_{OX} = 0 \). Its solution is \( \phi_0^{1/2} = -U_B^{1/2} + (U_B + \chi_m - \phi_s - \zeta + U_{OX})^{1/2} \). In both scenarios, once \( \phi_0 \) is obtained, \( \Delta U = e\sigma_m(\phi_0)/C_G \) is determined and then \( \Phi_{Bh} \) and \( \Phi_{Be} \) are determined accordingly.

We will estimate the relevant numerical values. If \( \Gamma \% \) of the CNT is covered with oxygen molecules \( O_2^{\delta^-} \), then \( \sigma_{ox}/e = -1.86 \times 10^{13} \Gamma \text{ cm}^{-2} \). Then, the contribution of \( \sigma_{ox} \) upon \( \Delta U \) is estimated to be \( 0.336 \alpha\Gamma\delta/e_r \text{ eV} \). With \( \alpha \sim 2-3 \text{ Å}, \Gamma \sim 10 \%, \delta \sim 0.01-0.1 \), and \( e_r \sim 10 \), the contribution is a few tenths of an electron volt. Considering \( E_G \sim 0.5 \text{ eV} \) for a familiar \((17,0)\) CNT [9], the present model successfully describes the reported effect of oxidation upon \( \Phi_B \) [2].

So far, we have assumed that the oxygen molecules are physisorbed, but it is instructive to examine the chemisorbed case [10]. In this case, \( \sigma_{ox} \) is no longer a constant, but depends on \( \phi_0 \) and \( \zeta \) such that \( \sigma_{ox}(\phi_0) = -en(\epsilon_0 - \phi_0 - \zeta)/\epsilon_0 \), where \( n\delta/e_0 \) is the number of energy levels per unit area with energies in the range \( d\epsilon \). Since \( \sigma_{ox}(\phi_0) \) is a straight line with a gradient \( -en/e_0 \), \( \sigma_{NT} + \sigma_{ox} \) is steeper and \( \phi_0 \) tends to be smaller in magnitude for a larger \( en/e_0 \). Thus, \( \phi_0 \) cannot be very different in air and in vacuum, and \( \Phi_B \) is eventually pinned [11]. This is contrary to the experimental results [2], and it is expected that the oxygen molecules are either physisorbed or chemisorbed weakly with a low \( n \) in the typical experimental situations.

We have proposed a model for the \( \Phi_B \) modulation in oxidation in the electrode – CNT system. The model considers a transition region at the Schottky junction and an appreciable potential can drop there. Oxidation increases this potential drop and therefore modifies \( \Phi_B \). We have explained the mechanism of low \( \Phi_{Bh} \) in air and high \( \Phi_{Bh} \) in vacuum successfully.

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References

a) CSC, Electronic address: yamada@nas.nasa.gov


[3] $V_G$ induces charge $-C_{NT}V_G$ in the channel, where $C_{NT}$ is a CNT capacitance, and this modifies the Fermi level. Thus, $\alpha = C_{NT}\left(C_{NT} + e^2D_0\right)$, where $D_0$ is a CNT state density at $V_G = 0$.


[11] The Fermi level pinning due to the large surface states in the device geometry of Fig. 3 is possible as discussed in F. Leonard and J. Tersoff, Phys. Rev. Lett. 84, 4693 (2000).
Figure Captions

FIG. 1. CNT FET characteristics in vacuum: (a) schematic channel conductance $g_d$ as a function of gate voltage $V_G$ in Ref. 2; (b) equilibrium band structure with the CNT conduction and valence edges at $V_{G1}$; (c) band structure at $V_{G2}$. CNT FET characteristics in air: (d) schematic $g_d(V_G)$ in Ref. 2; (e) band structures at $V_{G3}$; (f) band structure at $V_{G4}$.

FIG. 2. Band structures for metallic electrode – semiconducting CNT Schottky junction based on the conventional view: (a) in vacuum and (b) in air. Proposed band structures showing a potential drop $\Delta U$ in the transition region: (c) in vacuum and (d) in air. $a$ is the width, $\varepsilon_r$ is the dielectric constant, $\phi_s$ is the electron affinity, $\zeta$ is the Fermi level, $\chi_m$ is the work function, $\Phi_{Bh}$ is the hole Schottky barrier, and $O_2^{-}$ indicates negatively charged oxygen molecules.

FIG. 3. CNT FET with gate voltage $V_G$ in equilibrium: (a) real space charge distribution and (b) equivalent band structure along the arrow path above.

FIG. 4. Schematic plots of charge $\sigma$ as a function of band bending $\phi_0$: (a) $p$-CNT case and (b) $n$-CNT case. $\alpha_i$ and $\beta_i$ ($i = 0, 1, \text{or } 2$) are CNT charge lines, and $\kappa a$ and $\kappa b$ are electrode charge lines. Band structures are shown for operating points: (c) A0 for $p$-CNT in vacuum; (d) A2 for $p$-CNT in air; (e) B0 for $n$-CNT in vacuum; (f) B1 for $n$-CNT in air. $\phi_s$ is the electron affinity, $\zeta$ is the Fermi level, $\chi_m$ is the work function, $\Phi_{Bh}$ is the hole Schottky barrier, $\Phi_{Be}$ is the electron Schottky barrier, and $\sigma_{ox}$ is the negative charge on $O_2^-$. 
source $\text{CNT}$ drain

(a) vacuum

(b) $V_{G1} \leq V_{G2} \leq V_{G}$

(c) $-\alpha|eV_{G1}|$

(d) air

(e) $V_{G3} \leq V_{G4} \leq V_{G}$

(f) $-\alpha|eV_{G3}|$

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Fig. 1
Fig. 3

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(a) vacuum

(b) air

(c) vacuum

(d) air

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Fig. 2
p-type scenario

(a) \( k \alpha k \cdot \phi_s \cdot \zeta \cdot 0 \)
(b) \( k \alpha k \cdot \chi_m \cdot \phi_s \cdot \zeta \cdot 0 \)
(c) \( A_0 \) (p, vacuum)
(d) \( A_2 \) (p, air)
(e) \( B_0 \) (n, vacuum)
(f) \( B_1 \) (n, air)

n-type scenario

\( \sigma_{ox1} \)
\( \sigma_{ox2} \)

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Fig. 4