Size-Dependent Effects on Electrical Contacts to Nanotubes and Nanowires

François Léonard* and A. Alec Talin
Sandia National Laboratories, MS9161, Livermore, California 94551, USA
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Metal-semiconductor contacts play a key role in electronics. Here we show that for quasi-one-dimensional (Q1D) structures such as nanotubes and nanowires, side contact with the metal only leads to weak band realignment, in contrast with bulk metal-semiconductor contacts. Schottky barriers are much reduced compared with the bulk limit, and should facilitate the formation of good contacts. However, the conventional strategy of heavily doping the semiconductor to obtain Ohmic contacts breaks down as the nanowire diameter is reduced. The issue of Fermi level pinning is also discussed, and it is demonstrated that the unique density of states of Q1D structures makes them less sensitive to this effect. Our results agree with recent experimental work, and should apply to a broad range of Q1D materials.

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The early work of Schottky, Mott, and Bardeen has laid the course for much of the fundamental understanding and improvement in the performance of electrical contacts to bulk semiconductors. However, as new nanomaterials are explored for nanoelectronics, the fundamental aspects of contacts need to be reexamined due to the unique properties of nanostructures. An example is carbon nanotubes (NTs): despite much experimental work, it is still unclear whether the contacts are Schottky or Ohmic, with reports of Schottky contacts for Ti [1] and Ohmic contacts for Au [2] and Pd [3,4]. However, recent experimental work [5,6] has suggested that the type of contact depends on the NT diameter, with Schottky contacts for small diameter NTs and Ohmic contacts for large diameter NTs.

From a theoretical perspective, it has been demonstrated that Fermi level pinning (crucial in traditional semiconductors) is ineffective for quasi-one-dimensional nanostructures *end bonded* to metals [7]. For NTs *side contacted* by a metal, modeling has been used to extract Schottky barriers from experimental measurements [5], but has not addressed the origin of the Schottky barriers; and atomistic calculations have provided case-by-case studies [8–11]. However, a more general theoretical understanding for side contacts to quasi-one-dimensional (Q1D) structures is still missing, especially in light of the recent experimental findings.

In this Letter, we present a theoretical and modeling analysis of side contacts to nanotubes and nanowires. We show that the concepts developed for bulk metal-semiconductor contacts do not simply carry over to the nanoscale. In particular, band realignment due to charge transfer is weak due to the limited available depletion width. In NTs, this leads to relatively small and slowly varying Schottky barriers with NT diameter. In nanowires (NWs), there is a range of diameters with minimized Schottky barriers, providing optimal contact properties. We also demonstrate that in general, Q1D structures are much less sensitive to Fermi level pinning than their bulk counterparts. Finally, a conventional strategy for making Ohmic contacts is to heavily dope the semiconductor near the contact: we show that at typical dopings, the contact resistance increases rapidly as the nanowire diameter is decreased.

We begin by describing the contact geometry considered here. Figure 1(a) shows a sketch of a cross section of the contact consisting of a Q1D structure embedded in a metal. For explicit systems, we consider a single-wall NT, as shown in Fig. 1(b), or a solid nanowire as in Fig. 1(c). For the NT, the metal forms a cylindrical cavity of radius $R + s$ where R is the NT radius and $s = 0.3$ nm is the distance between the NT and the metal, while for the NW we consider a solid, continuum cylinder embedded in a perfect metal, with a sharp interface between the nanowire surface and the metal.

In the simplest picture, the difference between the metal Fermi level E_F and the semiconductor valence band edge E_v (the barrier for holes) is [Fig. 1(d)]

$$\Delta_0 = E_g + \chi - \Phi_m, \tag{1}$$

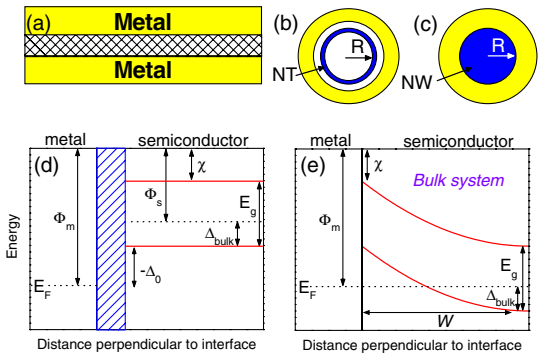

FIG. 1 (color online). Panel (a) shows a cross section of the contact along the length of the nanostructure. Panels (b) and (c) show radial cross sections for metal-nanotube and metal-nanowire contacts. Panel (d) shows the band alignment before charge transfer. In a bulk contact, panel (e), band bending over a distance W leads to a Schottky barrier Δ_{bulk}.

where Φ_m is the metal work function, χ is the semiconductor electron affinity, and E_g is the semiconductor band gap. A positive value for Δ_0 indicates a Schottky barrier, while a negative value indicates an Ohmic contact. Because the band gap decreases with increasing diameter for Q1D structures, the value of Δ_0 depends on the nanostructure diameter. The behavior of Eq. (1) for undoped NTs is shown in Fig. 2 for a value of $\Phi_m - \Phi_{\mathrm{NT}} = 0.4$ eV (typical of Pd), and using the relation $E_g = 2a\gamma/d$ between band gap and NT diameter d ($a = 0.142$ nm is the C-C bond length, $\gamma = 2.5$ eV is the tight-binding overlap integral, and Φ_{NT} is the NT work function assumed to be at midgap for an undoped NT). One problem with this picture (besides the fact that the physics is incomplete, as will be discussed below) is that Eq. (1) predicts large and negative values for Δ_0, signaling strong Ohmic contacts. However, it is clear that such strong Ohmic contacts are not observed experimentally.

In general, charge transfer between the metal and semiconductor leads to band realignment. At a bulk semiconductor junction [Fig. 1(e)] this charge transfer leads to the Schottky barrier

$$\Delta_{\mathrm{bulk}} = E_g + \chi - \Phi_s, \tag{2}$$

where Φ_s is the semiconductor work function. This relationship arises because, in the bulk system, a depletion width W perpendicular to the metal-semiconductor interface is created until the band lineup in Eq. (2) is obtained. However for Q1D structures, the depletion width depends *exponentially* on the doping [12] and is much longer than the device size for nondegenerate doping, leading to slowly varying bands outside of the contact; and for a three-terminal device the band bending in the channel is governed by the gate voltage. In either case, the band alignment is determined by that in the contact. But for a side-contacted Q1D structure, the semiconductor is only a few nanometers thick in the direction perpendicular to the metal-semiconductor interface; thus only a region of the order of the nanostructure cross section can be depleted,

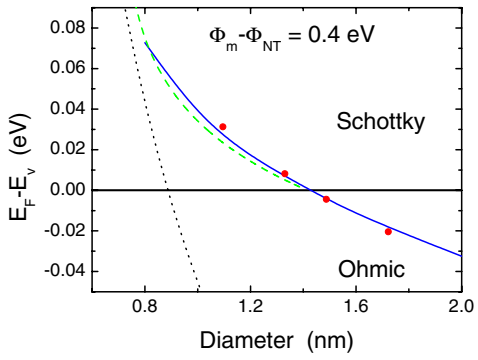

FIG. 2 (color online). Schottky barrier at nanotube-metal contacts for parameters typical of Pd. Dotted line is from Eq. (1), solid line is from Eqs. (3) and (4), dashed line is Eq. (6), and circles are calculated from the atomistic approach.

giving partial band realignment. The value of Δ will then be somewhere between Δ_0 and Δ_{bulk} (for an undoped NT or NW, $\Delta_{\mathrm{bulk}} = E_g/2$, which would always give relatively high Schottky barriers).

Nanotubes are an extreme example of this situation, since the possible "depletion width" is the size of the NT wall; the charge transfer and image charge in the metal create two nested hollow cylinders with opposite charge, and an associated electrostatic potential. The charge and potential must be self-consistent. We can capture this behavior using analytical models for the charge and potential. The charge per unit area on the NT is expressed as

$$\sigma = eN \int D_{\mathrm{NT}}(E + eV_{\mathrm{NT}}) f(E - E_F) dE, \tag{3}$$

where $D_{\mathrm{NT}}(E)$ is the NT density of states [13] shifted by the electrostatic potential on the NT, $f(E - E_F)$ is the Fermi function, and $N = 4/(3\sqrt{3}a^2)$ is the atomic areal density. We assume a uniform and sharp distribution of the charge on the NT, and all calculations presented in this Letter are for room temperature.

For the geometry of Fig. 1, solution of Poisson's equation gives the potential on the NT as

$$eV_{\mathrm{NT}} = -\sigma \frac{eR}{\varepsilon_0} \ln \frac{R+s}{R} = -\frac{e^2}{C}\sigma, \tag{4}$$

where ε_0 is the permittivity of free space and C is the capacitance per unit area between the metal and the NT. Equations (3) and (4) can be solved self-consistently for a given NT. In this model the electrostatic potential induced on the NT modifies the barrier to $\Delta = \Delta_0 - eV_{\mathrm{NT}}$. Figure 2 shows the results of such calculations for parameters typical of Pd. Clearly, the behavior is different from the simple expressions in Eqs. (1) and (2). Indeed, the bulk limit $\Delta_{\mathrm{bulk}} = E_g/2$ gives very large barriers, much too large to even appear on the scale of Fig. 2. The results suggest that there is a transition between Schottky and Ohmic behavior at a NT diameter around 1.4 nm, in agreement with recent experimental data for Pd contacts [5,6]. We have verified these predictions using an atomistic description of the NT based on a self-consistent, tight-binding Green's function formalism. As shown in Fig. 2, the results of such calculations indicate excellent agreement with the analytical approach introduced above.

To proceed further we focus on the small and positive Δ regime; approximation of the integral in Eq. (3) leads to

$$\sigma = \frac{eNa\sqrt{3}}{2\sqrt{2\beta}\pi^{3/2}R\gamma} \sqrt{\frac{E_g kT}{2}} e^{-\beta(\Delta/kT)} \tag{5}$$

with $\beta = 0.7$. Combined with Eq. (4) this gives the Schottky barrier

$$\Delta \approx \frac{kT}{\beta} \ln\left(\frac{\alpha\sqrt{\frac{E_g}{2kT}}}{\ln\alpha\sqrt{\frac{E_g}{2kT}} - \Delta_0/kT}\right), \tag{6}$$

where $\alpha = (e^2 N a\sqrt{3})/(2\sqrt{2\beta}\pi^{3/2} R\gamma C)$. The behavior of this function is plotted in Fig. 2, showing good agreement with the full calculation. The logarithmic dependence implies relatively slowly varying Δ, at least compared with Eq. (1). The NT diameter delimiting Schottky from Ohmic behavior is [14]

$$d \approx d_0\left(1 + \alpha\sqrt{\frac{kT}{\Phi_m - \Phi_{\mathrm{NT}}}}\right), \tag{7}$$

where d_0 is the crossover diameter that would be obtained from Eq. (1). Thus the crossover diameter is increased by $\delta d = \alpha\sqrt{\frac{kT}{\Phi_m - \Phi_{\mathrm{NT}}}} d_0$. Making ohmic contact to a wide range of NT diameters requires a small δd; this can be accomplished at low temperature, with a large metal work function, or with a large capacitance (giving a small α). Embedded contacts thus provide an advantage over planar contacts because of their larger capacitance.

We now consider side contacts to nanowires, where the possible depletion width increases with diameter, and the dependence of the band gap on diameter is different than in NTs. We model a NW with density of states

$$D_{\mathrm{NW}}(E) = \frac{\sqrt{2m^*}}{\pi\hbar}(E - E_g/2)^{-1/2}, \tag{8}$$

where m^* is the effective mass. For silicon NWs, it has been shown experimentally [15] that the band gap depends on diameter as $E_g = E_0 + C/d^2$, where $E_0 = 1.12$ eV and $C = 4.33$ eV nm^2. We consider the situation $\Phi_m - \Phi_{\mathrm{NW}} = 0.7$ eV typical of contacts to Si. Figure 3(a) shows the expected Schottky barrier heights from Eq. (1) which predict Ohmic contacts to NWs with diameters larger than 4 nm. To study the effects of charge transfer, we perform a self-consistent calculation of the charge and potential, using Eq. (8) to obtain the charge and solving Poisson's equation numerically in the NW to obtain the potential (we use an atomic volume density $N_v = 5 \times 10^{28}$ atoms/m^3).

Figures 3(b) and 3(c) show the self-consistent band bending for NWs of 2 and 10 nm radius. Clearly, the nanoscale dimension of the NWs prevents the bands from reaching their asymptotic value; instead, there is only a weak band bending present. To quantify the Schottky barrier height, we calculate the spatial average of $E_F - E_v(r)$; the results plotted in Fig. 3(a) indicate that the contact is always of Schottky character, with the barrier minimized at a diameter of about 4 nm. Thus, while in NTs the barrier height decreases monotonically with diameter, the behavior in other Q1D structures may be nonmonotonic, with a range of diameters providing optimal contact properties. We also note that, just as for NTs, the barrier heights are much smaller than the bulk limit $\Delta_{\mathrm{bulk}} = E_g/2$ (not shown in Fig. 3 for clarity).

In a bulk metal-semiconductor contact, metal-induced gap states (MIGS) lead to Fermi level pinning, and modification of the Schottky barrier height to Δ_{pin} [7]. To model this effect in side contacts to Q1D structures, we consider a

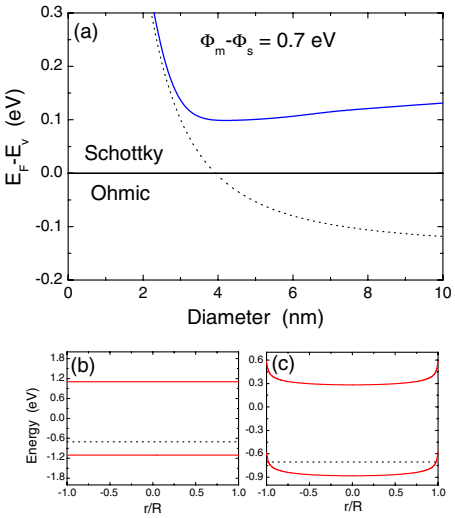

FIG. 3 (color online). Panel (a): Schottky barrier at nanowire-metal contacts for parameters typical of SiNWs. Dotted line is from Eq. (1) and the solid line is self-consistent calculation. Panels (b) and (c): Band bending across nanowires with diameters of 2 and 10 nm, respectively; dotted lines are the Fermi level.

radial pinning charge

$$\sigma_{\mathrm{pin}}(r) = D_0 N_A[E_F - E_N(r)]h(r), \tag{9}$$

where the neutrality level E_N is at midgap [i.e., $E_N(r) = -eV(r)$], $h(r) = e^{-r/l}$ for a NW and $h(r) = \delta_{r,R}$ for a NT, and $N_A = N$ for a NT and $N_A = N_v^{2/3}$ for a NW. We choose $l = 0.3$ nm, a typical value for metal-semiconductor interfaces [16]. We add this pinning charge to Eq. (3) or to the charge calculated from Eq. (8) and repeat our self-consistent calculations.

Figure 4(a) shows the Schottky barrier calculated for several NTs as a function of the density of gap states ($\Delta_{\mathrm{pin}} = E_g/2$). Clearly, there is a rapid onset of pinning at $D_0 \sim 0.1$ states/(atom $\cdot$ eV); this value of D_0 is rather large considering the van der Waals bonding of NTs to metals, and atomistic calculations [8,10] have obtained seemingly small values. Thus, as in end-bonded contacts, we expect that Fermi level pinning will play a minor role in side contacts to NTs.

Figure 4(b) shows the effects of Fermi level pinning on the barrier height in SiNWs. The results also indicate a value of $D_0 \sim 0.1$ states/(atom $\cdot$ eV) required to see pinning effects. For comparison, the inset in this figure shows the same calculation for a bulk metal-semiconductor interface with the same parameters, indicating that only 0.002 states/(atom $\cdot$ eV) are needed to reach the onset of pinning. Thus, the Q1D system requires almost 2 orders of magnitude larger density of pinning states compared with the bulk interface.

The origin of this behavior can be traced to the unique density of states of Q1D systems. Indeed, for Si, we can repeat the analysis leading to Eq. (5) using the density of

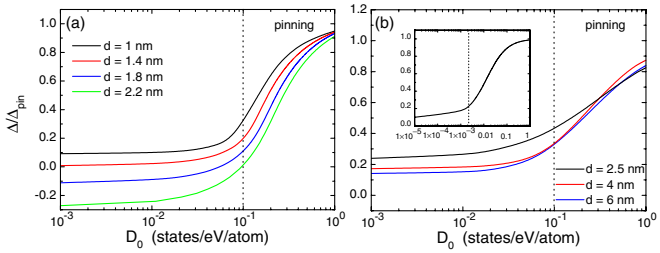

FIG. 4 (color online). Schottky barrier as a function of the density of gap states for several NTs (a) and NWs (b). The inset in (b) shows the behavior for a planar metal-semiconductor contact.

states for the NW and for the bulk system $[D_{\mathrm{bulk}}(E) = \sqrt{2}(m^*)^{3/2}(\pi^2\hbar^3)^{-1}\sqrt{E - E_g/2}]$. This leads to the ratio $\sigma_{\mathrm{NW}}/\sigma_{\mathrm{bulk}} = (2\pi N_v^{1/3}\beta)/(m^*kT)$. The appearance of the kT factor in the denominator is entirely due to the Q1D density of states of the NW and the presence of a van Hove singularity at the band edge. At room temperature, we find that $\sigma_{\mathrm{NW}}/\sigma_{\mathrm{bulk}} > 100$; thus the MIGS are competing with a much larger charge density in the Q1D system.

Our discussion has so far focused on the situation of low doping, where the strategy for making Ohmic contacts is by selection of a metal with an appropriate work function. In traditional metal-semiconductor contacts, an alternative approach is to heavily dope the semiconductor, and rely on tunneling through the Schottky barrier to reduce the contact resistance and obtain Ohmic contacts. To address the feasibility of this approach for contacts to NWs, we repeat our self-consistent calculations for the Si NW, focusing on the situation where the metal Fermi level is in the middle of the NW band gap at the interface, and adding a uniform doping charge of 1×10^{19} cm^{-3}. Figure 5 shows the band-bending in the presence of this doping charge for NWs of 40 and 10 nm diameters. We calculate the contact conductance from

$$G \sim \int_{E_c^{\min}}^{\infty} T(E)\left(-\frac{\partial f}{\partial E}\right)dE, \qquad (10)$$

where the tunneling probability $T(E)$ is obtained from the WKB approximation. The normalized contact resistance is then G_∞/G, where G_∞ is the conductance in the limit of large diameters. The behavior of the normalized resistance as a function of NW diameter is shown in Fig. 5(c), indicating a rapid increase of the resistance with decrease in diameter. The origin of this behavior is the increased tunneling distance and reduced range of tunneling energies because of the poor band bending. One implication of this result is that different diameter NWs will require different doping levels to achieve the same contact quality.

In summary, we find that the concepts developed to describe traditional metal-semiconductor interfaces fail to properly account for the properties of contacts to Q1D

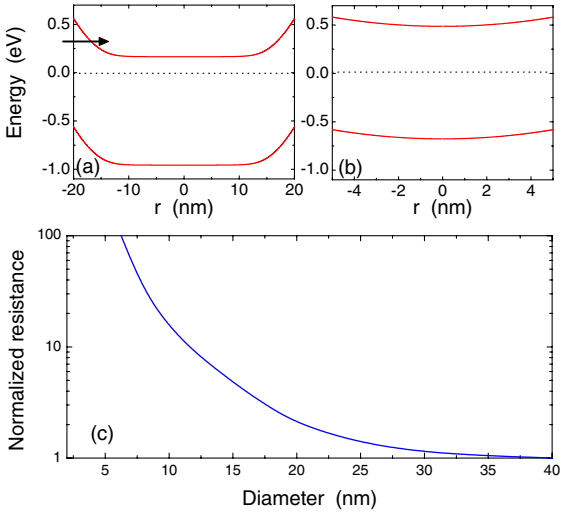

FIG. 5 (color online). Band bending across Si NWs with doping of 1×10^{19} cm^{-3} for diameters of 40 (a) and 10 nm (b). The arrow indicates tunneling of electrons through the Schottky barrier. The normalized resistance is shown in (c) as a function of NW diameter.

structures. Optimizing device performance will not only require selecting Q1D structures for their behavior in the channel, but also for their contact properties. We expect that our results will be applicable to a broad range of Q1D structures.

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*Electronic address: fleonar@sandia.gov

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