Modeling of electronic transport in scanning tunneling microscope tip - carbon nanotube systems

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A model is proposed for two observed current-voltage (I-V) patterns in a recent experiment with a scanning tunneling microscope tip and a carbon nanotube [Collins *et al.*, Science **278**, 100 (1997)]. We claim that there are two mechanical contact modes for a tip (metal) -nanotube (semiconductor) junction (1) with or (2) without a tiny vacuum gap (0.1 - 0.2 nm). With the tip grounded, the tunneling case in (1) would produce large dI/dV with $V > 0$, small dI/dV with $V < 0$, and $I = 0$ near $V = 0$ for an either n- or p-nanotube; the Schottky mechanism in (2) would result in $I \neq 0$ only with $V < 0$ for an n-nanotube, and the bias polarities would be reversed for a p-nanotube. The two observed I-V patterns are thus entirely explained by a tip-nanotube contact of the two types, where the nanotube must be n-type.

Recently, current-voltage (I-V) characteristics have been reported by Collins *et al.* for a system with a scanning tunneling microscope (STM) tip and a carbon nanotube at room temperature [1]. The STM tip was driven forward into a film of many entangled nanotubes on a substrate, and then was retracted well beyond the normal tunneling range. At a distance of ~ 0.1 μm above the surface, there was usually an electronic conduction between the tip and the film since nanotubes bridged the two regions. At ~ 1 μm, only one nanotube remained occasionally, and the electronic conduction was still maintained. One end of the nanotube continued sticking to the tip during the retraction, while the other consistently stayed in the film. I-V characteristics for this tip-nanotube system had two different patterns for low (< 1.95 μm) and high (1.98 μm) tip-to-film distances as schematically shown in Figs. 1(a) and 1(b). The lower-distance cases showed large dI/dV with $V > 0$, small dI/dV with $V < 0$, and $I = 0$ near $V = 0$ (type-I), while the high-distance case showed rectification, i.e., $I \neq 0$ only with $V < 0$ (type-II), if the tip was grounded (different bias definition from [1]). This article proposes a physical mechanism to explain the observed I-V patterns.

We consider that the observed characteristics strongly reflected the nature of the tip (metal) - nanotube (semiconductor) contact. The other end of the nanotube was entangled well in the film, and simply provided a good Ohmic contact. We will argue that there are two different mechanical contact modes - vacuum gap (right) and touching (right) modes as in Fig. 1(c), depending on the presence or absence of a tiny vacuum gap d ~ 0.1 - 0.2 nm at the junction. These modes are related to physisorption and chemisorption, respectively. Once admitting their existence, it is naturally shown that I-V characteristics are type-I in the vacuum gap mode, and type-II in the touching mode. We will show that the nanotube had to be an n-type semiconductor, contrary to often observed p-type semiconducting nanotubes in the field-effect-transistor (FET) applications [3].

Experimentally, the STM tip was not placed at the end of the nanotube as if it were an extension, but contacted the side of the nanotube so that the tip and nanotube surfaces faced each other. Thus, the one-dimensional cylindrical junction effects [4] are not relevant here. Additionally, Ref. 5 shows that nanotubes will generally flatten on a substrate due to the van der Waals interaction. A nanotube will flatten at the STM tip surface in both contact modes shown in Fig. 1. Therefore, the tip-nanotube junction is well approximated by the traditional planar junction model [2].

The band diagrams are shown in Fig. 1 for several points in the *I-V* patterns: (d) - (f) for type-I in the vacuum gap mode (left) and (g) - (i) for type-II in the touching mode (right). In the metal, E_{FM} is the Fermi energy and o_M is the work function. In the semiconductor, χ is the electron affinity, E_{FS} is the Fermi energy, and E_G is the band gap. E_c and E_v are conduction and valence band edges, respectively, and are dependent on the applied voltage V after the tip is grounded. ϕ_n and ϕ_p are Schottky barriers and $\xi = E_{FS} - E_v$. At (d), valence-band electrons tunnel to the tip with $V < 0$, resulting in smaller dI/dV. (e) is a thermal equilibrium with $V = 0$. At (f), tip electrons tunnel to the conduction band with $V > 0$, resulting in larger dI/dV. The vacuum gap provides flexibility for E_c and E_v to align freely with E_{FM} by absorbing the necessary voltage drop for given V. In the touching mode, ϕ_n and ϕ_p are fixed regardless of V. The Schottky forward transport occurred at the same bias polarity as the *valence*-band tunneling of (d) did (this is independent of the polarity definition). Thus, (g) follows with $V > 0$, and the nanotube has to be *n*-type. (h) is a thermal equilibrium. (i) is a reverse condition with $V > 0$ with practically no current. If the Schottky forward transport had occurred at the same polarity as the *conduction*-band tunneling of (f) (in our case $V > 0$), then the nanotube would have been *p*-type.

In the vacuum gap mode, we assume that the total energy E and the parallel-momentum $k_\rho = (k_x^2 + k_y^2)^{1/2}$ are conserved in the tunneling [6], where k_x and k_y are transverse (quantized) and

longitudinal (continuous) momenta, respectively. Nanotubes are finite in the x direction, and k_x is not exactly conserved, while k_y is [7]. Both are conserved only for infinitely wide nanotubes. We consider a *semiconducting* (17,0) nanotube with a diameter 1.33 nm, which is the closest to the experimental estimation of 1.36 nm [1] in the zigzag tube families [9]. The nanotube is wide enough that subbands are treated as a group in a k_ρ-integration with the effective mass m_i for band i ($i = c, v$). We have evaluated m_i by averaging the inverse masses for 17 subbands, and found $\alpha_c = \alpha_v = 0.216$, where $\alpha_i = m_i/m$ with m being the vacuum electron mass. The current I_i via band-i tunneling at zero temperature is given by [6,8],

$$I_i = \frac{4\pi meS}{h^3}\int_{E_{FM}-eV}^{E_{FM}} dE\,\theta[\pm\{E - E_i(V)\}]\int_{E(1\mp\alpha_i)\pm\alpha_i E_i(V)}^{E} dW D(W), \qquad (1)$$

where the integrations are performed for E and normal (z) energy W (converted from the k_ρ integration since E - W is related to k_ρ) in the metal. The lower limit of W integration cannot reach E_i due to the E-$k_\rho$conservation discussed above. e is the unit charge, S is the tip-nanotube overlap area, h is the Planck constant, and θ is a step function. D is a transmission coefficient and assumed to depend only on W [8]. $E_G = 0.54$ eV and $\chi = 4.6$ eV (graphite ϕ_M) - $E_G/2 = 4.3$ eV for a (17,0) nanotube [9,10], and $\phi_M = 4.5$ eV (tungusten tip). These numbers define the vacuum barrier height, and $D(W)$ is calculated with a WKB approximation [6]. Image potential [2,6] is not considered, and the semiconductor band bending [2,8] is neglected, but they do not change our qualitative results. S, d, and ξ will be determined to fit the experimental I-V data best.

Figure 2 shows an analysis for a tip-to-film distance of 1.85 μm [1]. ξ shifts the entire I-V curve horizontally and the best fit is obtained for $\xi/E_G = 0.65$ (> 0.5). This is consistent with our conclusion of n-type nanotube. For very large d such as 0.40 nm, dI/dV asymmetry for opposite polarities are more enhanced than the experiment, and S is unreasonably large ~ 4000 nm^2. This

is certainly not the case. For $d \sim 0.1$ - 0.2 nm with $S \sim 3$ - 34 nm^2, the curves are indistinguishable. d is measured from the natural distance defined by the surface bonding, and there is no lower limit. S should be around $10^{0\text{-}1}$ nm^2. Thus, these are all likely candidates, and we will not narrow it down further. The calculated current is smaller than the measured one, and the measured voltage interval ΔV for $I = 0$ seems smaller than $E_G/e = 0.54$ V. E_G sharply depends on the diameter and a large deviation from this value is not likely (e.g., $E_G = 0.4$ eV for a diameter as large as 1.8 nm [10]). Since the semiconductor band bending reduces ΔV effectively [8], it could explain this discrepancy. The experiment at room temperature also reduces ΔV, and would be responsible for part of it. We do not explicitly include a series resistance R_S representing the bulk film resistance and the film-electrode contact resistance, etc. R_S is implicitly included in d and S. Overall fitting is reasonable, and the results correctly recover large dI/dV with $V > 0$ and small dI/dV with $V < 0$, one of the key experimental findings [1].

Figure 3 shows an analysis for a tip-to-film distance of 1.98 μm [1]. We will explicitly include R_S in this case. In an equivalent circuit with a Schottky diode and R_S, the diode current I_D, the diode voltage V_D, and the total voltage V are related by $I_D = -I_0[\exp(-\beta V_D) - 1]$ and $V = V_D + I_D R_S$ with β the inverse temperature. I_0 is a constant related to S and ϕ_n. The diode-only characteristics (V_D, I_D) are plotted in Fig. 3 with $I_0 = 3.53 \times 10^{-18}$ A, resulting in a discrepancy. We thus introduce $R_S = 1.54$ MΩ, and plot the characteristics ($V_D + I_D R_S$, I_D). This recovers the experiment well.

The experimental current level in Fig. 3 is smaller than that in Fig. 2. When the tip-to-film distance is low, the tip-nanotube binding will be weak (physisorption) and there will be a vacuum gap, so that S will be large to support the tension on the nanotube from the film. As the tip-to-film distance is higher, the tip-nanotube binding will be stronger (from physisorption to chemisorp-

tion) and S can be smaller. This is because the tension always tends to reduce S by pulling the nanotube down. S will be minimized in the touching mode where the binding is strongest. In fact, we can recover the above $I_0 \sim 3 \times 10^{-18}$ A by, e.g., $S \sim 0.1$ nm^2 and $\phi_n \sim 0.5$ eV ($< E_G$) using the Richardson constant $A^* \sim 10^1$ A/cm^2/K^2 in $I_0 = SA^*T^2\exp(-\beta\phi_n)$ [2], where T is the temperature. S and ϕ_n in these ranges are possible. For further investigation, S, ϕ_n, and A^* need to be determined experimentally.

Similar I-V characteristics to type-I here have also been observed for drain current vs. drain voltage in nanotube FETs [3]. However, some results were not due to the scenario discussed here, but due to the Coulomb blockade mechanism [11,12] for shorter nanotubes (~ 0.1 μm) at much lower temperatures (~ 4.2 K). Ref. 13 reported such an example. We have shown that the nanotube was n-type. It was hanging in air throughout the experiment [1]. On the other hand, nanotubes placed on a silicon-dioxide surface in the FET applications [3] were consistently p-type regardless of the lengths (0.3 - 3 μm). Contact electrodes probably could not provide holes everywhere in long nanotubes. The observed p-type behavior would be related to the silicon-dioxide surface in the FET structure.

In summary, the observed experimental I-V characteristics [1] for the STM tip-nanotube system are explained with a tip-nanotube contact model. In the vacuum gap mode, we expect different dI/dV at opposite bias polarities and $I = 0$ near $V = 0$ reflecting the conduction- and valence-band tunneling. In the touching mode, the I-V characteristics are rectifying, because of the usual Schottky mechanism. We have argued that the Schottky forward transport occurred at the same bias polarity as the valence-band tunneling did in the experiment, and concluded that the nanotube was a n-type semiconductor.

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References

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[1] P. G. Collins, A. Zettl, H. Bando, A. Thess, and R. E. Smalley, Science **278**, 100 (1997).

[2] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981).

[3] S. J. Tans, A. R. M. Verschueren, and C. Dekker, Nature **393**, 49 (1998); R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph. Avouris, Appl. Phys. Lett. **73**, 2447 (1998); T. Yamada, Appl. Phys. Lett. **76**, 628 (2000); C. Zhou, J. Kong, and H. Dai, Appl. Phys. Lett. **76**, 1597 (2000).

[4] F. Leonard and J. Tersoff, Phys. Rev. Lett. **83**, 5174 (1999).

[5] T. Hertel, R. E. Walkup, and Ph. Avouris, Phys. Rev. B **58**, 13870 (1998).

[6] C. Duke, *Tunneling in Solids*, Suppl. 10 of *Solid State Physics*, edited by F. Seitz and D. Turnbull, (Academic, New York, 1969); J. Bono and R. H. Good, Jr., Surf. Sci. **175**, 415 (1986).

[7] P. Delaney and M. Di Ventra, Appl. Phys. Lett. **75**, 4028 (1999).

[8] R. M. Feenstra and J. A. Stroscio, J. Vac. Sci. Technol. B **5**, 923 (1987).

[9] R. Saito, M. Fujita, G. Dresselhouse, and M. S. Dresselhouse, Phys. Rev. B **46**, 1804 (1992), M. S. Dresselhaus, G. Dresselhouse, and P. C. Eklund, *Science of Fullenes and Carbon Nanotubes* (Academic, San Diego, 1996).

[10] J. W. Mintimore and C. T. White, Carbon **33**, 893 (1995). The diameter of 1.3 nm was directly measured with STM in L. C. Venema, J. W. G. Wildöer, J. W. Janssen, S. J. Tans, H. L. J. Temminic Tuinstra, L. P. Kouwenhoven, C. Dekker, Science **283**, 52 (1999).

[12] D. V. Averin and K. K. Likharev, J. Low Temp. Phys. **62**, 345 (1986); A. Bezryadin, A. R. M. Verschueren, S. J. Tans, and C. Dekker, Phys. Rev. Lett. **80**, 4036 (1998).

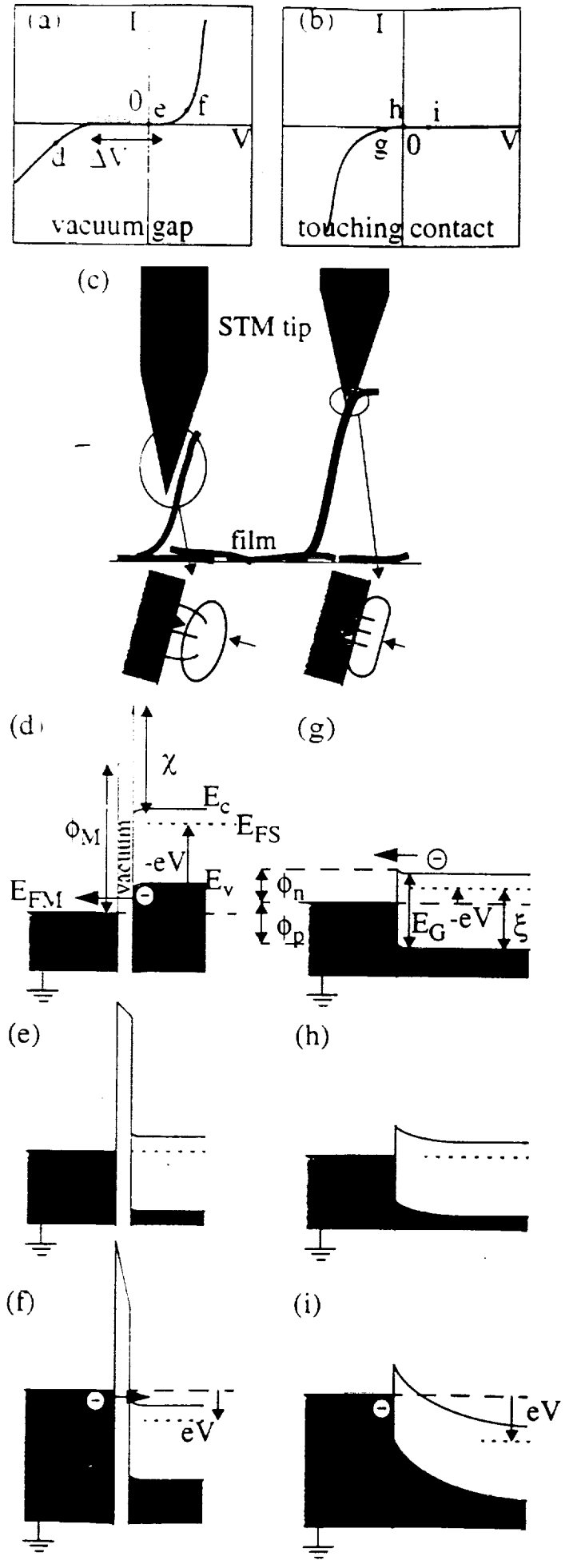
[13] H. R. Shea, R. Martel, T. Hertel, T. Schmidt, and Ph. Avouris, Microelectronic Engineering **46**, 101 (1999).

Figure Captions

FIG. 1. STM tip nanotube system with two mechanical contact modes: (a) type-I and (b) type-II *I-V* patterns. (c) schematically shows the vacuum gap (left) and touching (right) modes. (d) - (i) are band structures for operation points in the *I-V* patterns: (d) valence-band tunneling ($V < 0$), (e) equilibrium ($V = 0$), (f) conduction-band tunneling ($V > 0$), (g) Schottky forward ($V < 0$), (h) equilibrium ($V = 0$), and (i) Schottky reverse ($V > 0$), where the STM tip is grounded.

FIG. 2. *I-V* characteristics with experimental data for a tip-to-film distance of 1.85 μm of Ref. 1, analyzed with the tunneling formula in the vacuum gap mode.

FIG. 3. *I-V* characteristics with experimental data for a tip-to-film distance of 1.98 μm of Ref. 1, analyzed with the Schottky formula in the touching mode.


(a)
I
0
e
f
V
d
ΔV
vacuum gap
(b)
I
h
i
g
0
V
touching contact
(c)
STM tip
film
(d)
(g)
χ
E_c
E_FS
φ_M
vacuum
-eV
E_v
E_FM
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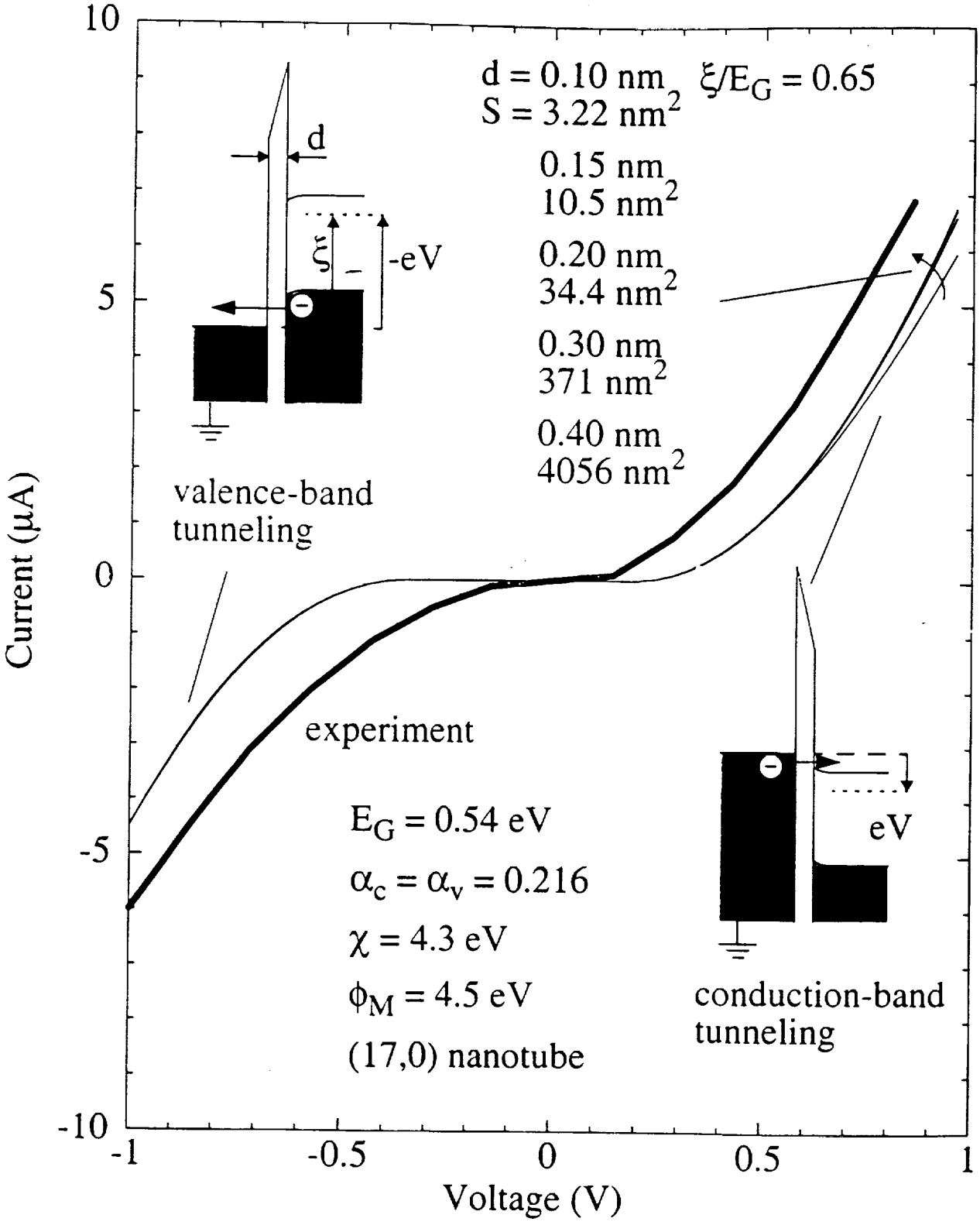
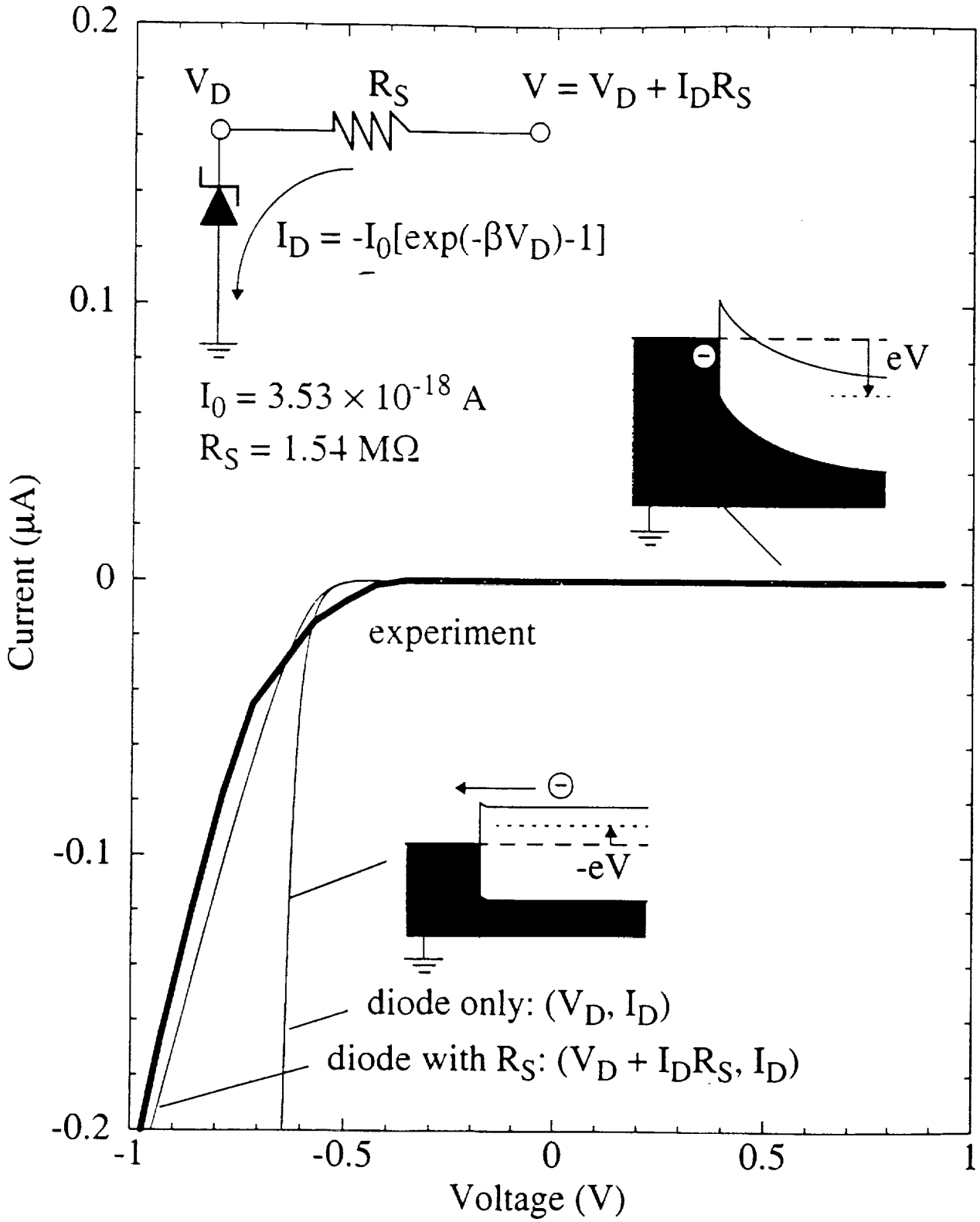
φ_p
E_G
-eV
ξ
(e)
(h)
(f)
(i)
eV
eV

Fig. 1


10
5
0
-5
-10
-1
-0.5
0
0.5
1
Current (μA)
Voltage (V)
d = 0.10 nm ξ/E_G = 0.65
S = 3.22 nm²
0.15 nm
10.5 nm²
0.20 nm
34.4 nm²
0.30 nm
371 nm²
0.40 nm
4056 nm²
d
ξ
-eV
valence-band
tunneling
experiment
E_G = 0.54 eV
α_c = α_v = 0.216
χ = 4.3 eV
φ_M = 4.5 eV
(17,0) nanotube
eV
conduction-band
tunneling


0.2
0.1
0
-0.1
-0.2
-1
-0.5
0
0.5
1
Current (μA)
Voltage (V)
V_D
R_S
$V = V_D + I_D R_S$
$I_D = -I_0[\exp(-\beta V_D)-1]$
$I_0 = 3.53 \times 10^{-18}$ A
$R_S = 1.54$ MΩ
eV
-eV
experiment
diode only: (V_D, I_D)
diode with R_S: ($V_D + I_D R_S$, I_D)