Transport in carbon nanotube *p-i-n* diodes

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Single-walled carbon nanotube diodes are fabricated in a split-gate geometry with electron (n) and hole (p) regions separated by a central region. With the central region gated p or n type the diodes "leak" at low voltages, likely due to tunneling across the smaller depletion region. With the central region intrinsic, nearly ideal diode behavior is observed. Comparison to theory for a one-dimensional diode yields the band gap of the tube and the transmission coefficient through the junction. In reverse bias, the breakdown voltage depends weakly on temperature and nanotube diameter. Comparisons are made to predictions for Zener tunneling and avalanche breakdown.
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Individual semiconducting carbon nanotubes (CNTs) have been shown to make excellent channels for both p- and n-type field effect transistors. Recently, Lee *et al.* fabricated CNT diodes using a split-gate geometry.[1] One side of the CNT is gated p type and the other side n type, forming a p-n junction separated by an intrinsic (i) region. They demonstrated that at room temperature these p-i-n devices show rectification consistent with expected diode behavior and that the forward bias characteristics at low bias are well described by the standard diode equation. In this letter, we study the temperature, bias, and gate voltage dependence of gated p-n junction diodes. In forward bias, we compare our results to those predicted for a one-dimensional semiconductor p-n junction and find excellent agreement. In reverse bias, we compare to theories of Zener and avalanche breakdown.

Our CNT split-gate devices are fabricated on highly doped Si wafers (see Fig. 1) with Mo gates in the oxide layer.[1] The CNTs are grown by chemical vapor deposition and have typical diameters of 1–3 nm, as measured by atomic force microscopy. The transistor characteristics of the devices are first measured by sweeping the Mo split gates (V_1 and V_2) and the global Si back gate (V_G) together. All of the devices used in these experiments show a substantial "off" region between the p- and n-type regions. The conductance in the n-type region is enhanced by pumping under vacuum for 2 h or more.[1] The n-type current is nonlinear in V_{SD} and is often only evident with large biases (e.g., $V_{SD} > 0.5$ V). At ambient temperatures, the device transfer characteristics show significant hysteresis, most likely due to surface water.[2] The hysteresis is largely frozen out at reduced temperatures.

Figure 1 shows a typical I-V_{SD} curve from a device at 20 K with the split gates oppositely biased. The device is strongly rectifying, turning on at less than 1 V in the forward bias direction, but with no significant current under reverse bias until about −9 V. The effect of varying the back gate voltage is shown in Fig. 2. The device I-V_{SD} behavior is significantly different when V_G is grounded (i.e., 0 V) and when it is equal to V_1 or V_2. In the former case the region of the CNT between the split gates is intrinsic (p-i-n), whereas in the latter cases this region is p or n type (p-p-n or p-n-n). In the p-p-n and p-n-n configurations the device "leaks" under both forward and reverse biases; that is, it begins conducting at much lower voltages than in the p-i-n configuration. The good diode behavior, like that seen in Fig. 1, requires a significant intrinsic region between the p and n regions. In the rest of this letter, we will primarily focus on the p-i-n region.

Figure 3 (inset top left) shows the I-V_{SD} curves in forward bias for a nanotube diode of approximate diameter 1.6 nm at two temperatures. At low bias, the current is exponential in temperature, with a slope that depends on T. At higher current the data fall below this exponential increase. From measurements of many devices, we find that the crossover between these regimes depends on the temperature and gate voltage, but typically occurs for $I \sim 1$ nA. Figure 3 shows I-V_{SD} curves at a variety of temperatures in the initial exponential region. The inset shows that the inverse of the slope varies linearly with T: $\alpha = dV/d\ln(I) \sim 1.2k_BT$.

Previously, Lee *et al.* observed similar exponential behavior with V at room temperature.[1] They fit their data to the ideal diode equation, $I = I_0(\exp(eV/nk_BT) - 1)$, to determine the parameter n. Here, we use measurements over a wide

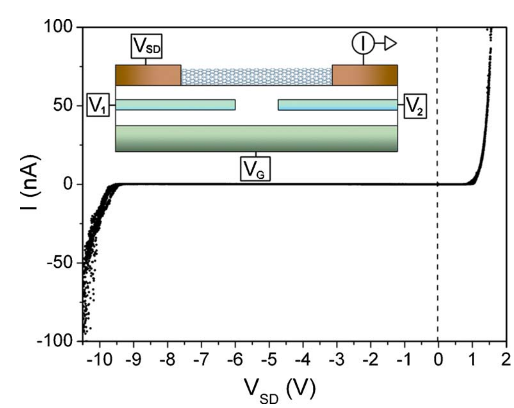

FIG. 1. (Color online) I-V_{SD} curve for a typical device ($V_{1/2} = \pm 8$ V, V_G grounded, $T = 20$ K). Inset: Device schematic.

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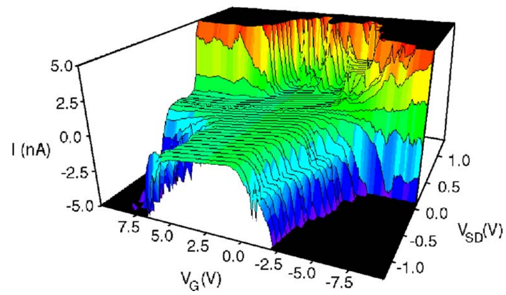

FIG. 2. (Color online) I-V_G-V_{SD} plot for a typical device ($V_{1/2}=\pm 10$ V, $T=120$ K).

TABLE I. Characteristics of four devices.

D[a] (nm)	E_g (eV)	$\Im_0$	n[b]	V_{BR}[c] (V)
1.2	0.62	0.3	1.2	7.3
1.6	0.51	0.2	1.2	5.9
2.7	0.30	0.1	1.8	5.1
3.2	0.25	0.3	1.5	4.9

[a] ±0.3 nm.
[b] $V_g=0$ V.
[c] $T=200$ K.

range of temperatures in conjunction with a diode model based on the one-dimensional Landauer formula to extract all the important parameters of the device.

Ignoring any recombination between the electron and hole bands, the current is given by

$$I \approx (4e/h)\int_{-\infty}^{\infty} \Im(E,V)[f_D(E) - f_S(E-eV)]dE. \quad (1)$$

We model the diode as having a transmission coefficient $\Im_0$ for energies above the band gap (for electrons) or below the band gap (for holes). Neglecting tunneling and assuming E_g and $eV \gg k_BT$, a straightforward calculation yields

$$I \approx (8ek_BT/h)\Im_0 \exp[(eV/n - E_g)/k_BT], \quad (2)$$

where $n \geq 1$ is a phenomenological factor that relates the applied voltage to the lowering of the effective barrier for electrons and holes. In the ideal case, $n=1$.

Comparison with the data in Fig. 3 the inset yields $n=1.2$ for this device. Equation (2) also predicts that plots of $I/(8ek_BT/h)$ vs V taken at different temperatures will all meet at a single voltage and current given by $V=nE_g/e$ and $I/(8ek_BT/h)=\Im_0$. The data indeed exhibit this behavior at $V=0.61$ V, $I=0.2\times(8ek_BT/h)$, allowing us to infer the band gap $E_g=0.61$ eV/1.2=0.51 eV and the transmission coefficient $\Im_0 \approx 0.2$. Data for four different CNTs with varying diameters are shown in Table I.

The band gap obtained from the transport measurements can be compared with the theoretical prediction of $E_g(\text{theory})=0.7$ eV/d [nm]. For the $d=1.6$ nm tube of Fig. 3, this gives $E_g(\text{theory})=0.44$ V, in reasonable agreement with the measured value of 0.51 V. Furthermore, the inferred band gaps in Table I scale accurately with the tube diameter. The good agreement clearly demonstrates that low bias I-V_{SD} curves for these diodes provide a direct measure of the band gap of the CNT.

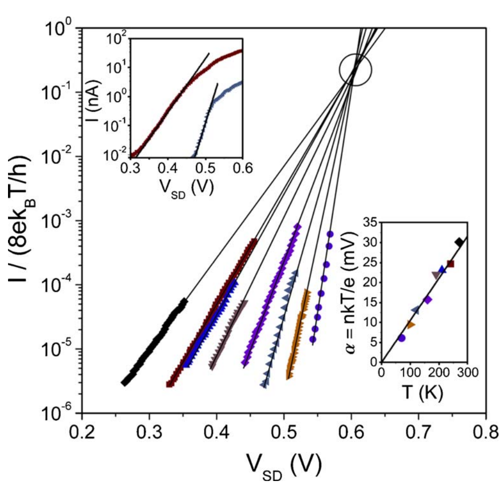

FIG. 3. (Color online) I-V_{SD} curves in the low forward bias regime at various temperatures. Inset top: Full I-V_{SD} curves in forward bias at $T=240$ K (■) and 120 K (◀). Inset bottom: Temperature dependence of the inverse slope $\alpha=dV/d\ln(I)$ of the I-V_{SD} curves.

The inferred transmission coefficient $\Im_0 \approx 0.2$ indicates that the motion of carriers across the junction region and to the other contact is quite efficient. We note that there are two parts to this process. First the electron or hole must traverse the ~1 μm long depletion region. Second, when it emerges as a minority carrier on the other side, it must recombine or diffuse to the other contact approximately 1–2 μm away before it falls back down the large potential barrier it surmounted. Phonon scattering lengths in semiconducting nanotubes have been measured to be in the 100 nm–1 μm range, depending on the temperature and the energy of the electron.[3] The electron-hole recombination length is not known, but optical measurements in light-emitting nanotube devices show a recombination length on the scale of microns.[4] Given that the sizes and scattering lengths are all of the same order, a value of $\Im_0 \approx 0.2$ is quite reasonable. A similar value was obtained in a p-n-p device geometry by Minot *et al.*[5]

The factor $n=1.2$ is similar to that obtained by Lee *et al.* from fits to the ideal diode equation at room temperature.[1] Our results confirm explicitly this thermal activation form over a wide temperature range. The deviation from the ideal value $n=1$ could be the result of a number of effects. In standard diode theory, n takes on values from 1 to 2, 1 being the limit of no recombination in the depletion region and 2 being the limit of complete recombination.[6] Alternately, disorder in the junction may make the bottleneck for transport somewhere in the depletion region, and there will be a lever arm relating the change in the barrier height with voltage. Recently Lee *et al.* found $n=1$ for suspended tubes.[7] This is consistent with both of the models above, since suspended tubes likely have less disorder[8,9] and less recombination centers.

We briefly comment on the forward bias curves at higher bias. Figure 4 shows the measured I-V_{SD} curves at higher currents. The solid lines are fits to the data using the combination of a series resistor and an exponentially increasing current, following Lee *et al.*[1] While the fits are often reasonable, the inferred slopes $\alpha=dV/d\ln(I)$ do not agree with the predictions of Eq. (2). Instead, we see a linear dependence of α on temperature but with an offset. The same statements are true for measurements in the p-n-n or p-p-n regions at *all* current levels. We therefore conclude that the thermally activated transport behavior described by Eq. (2) is only observed in p-i-n diodes at low currents.

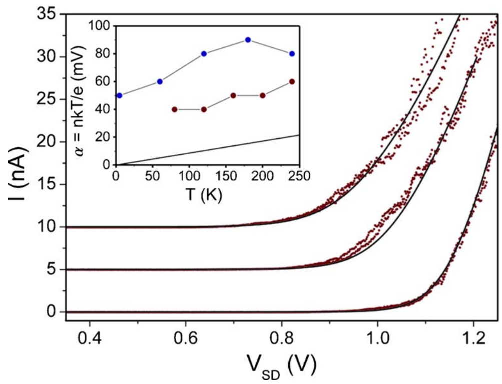

FIG. 4. (Color online) Fits of the ideal diode equation with a series resistor (1–6 MΩ) in the high forward bias regime at 80, 160, and 240 K (bottom to top, offset for clarity). Inset: α for two different devices. The solid line indicates the expected temperature dependence for an ideal diode.

We now turn to the reverse bias characteristics in the *p-i-n* region. We define a breakdown voltage V_{br} as the voltage under reverse bias at which $R=V/I\sim 1$ GΩ. From the analysis of curves similar to that shown in Fig. 1, we determine V_{br} as a function of CNT diameter and temperature (see Fig. 5). The breakdown voltage is in the range of 4–9 V for all of the devices measured. It grows with decreasing CNT diameter and with decreasing temperature. In the breakdown region, the current rises approximately exponentially with bias: $I=A\exp(V/\alpha)$, where α is typically 50–100 mV.

There are two main mechanisms for reverse bias breakdown in standard semiconductor diodes: interband (Zener) tunneling and avalanche breakdown.[6] We first consider Zener tunneling. The transmission probability for tunneling through the gap can be estimated using the WKB approximation:[10,11]

$$\Im = \exp\left[-\frac{2}{\hbar}2\int_o^{t/2}(2m\varepsilon x)^{1/2}dx\right] = \exp\left[-\frac{4}{3\sqrt{2}\hbar}\frac{E_g^2}{v_F\varepsilon}\right], \qquad (3)$$

where $\varepsilon=(E_g+V)/L$ is the electric field in the junction region and $t=E_g/\varepsilon$ is the distance that the electron must tunnel. Using Eq. (3), we can predict the threshold voltage at which the junction resistance is 1 GΩ:

$$V_{br}(\text{Zener}) \approx (75\ \text{V})(L\ [\mu\text{m}]/d\ [\text{nm}]^2) - E_g. \qquad (4)$$

In Fig. 5, the experimentally measured values are smaller than those predicted by Eq. (4) assuming $L\sim 1$ μm; a channel length $L\sim 100$ nm would bring the prediction more in line with the measured values. However, the diameter dependence is much weaker than predicted by Eq. (4) and the measured inverse slopes $\alpha=dV/d(\ln I)=50-100$ mV of the exponential turn-on are significantly smaller than those derived from Eq. (3): $\alpha=V_{br}/\ln(\Im_{br})\approx V_{br}/15$. Zener breakdown voltages typically decrease with increasing temperature due to the change in the band gap with temperature. This effect in CNTs is too small to explain the measured shifts.[12] For all these reasons, it is unlikely that the breakdown is by Zener tunneling in the bulk of the depletion region, although tunneling through imperfections or places where the electric field is high cannot be ruled out.

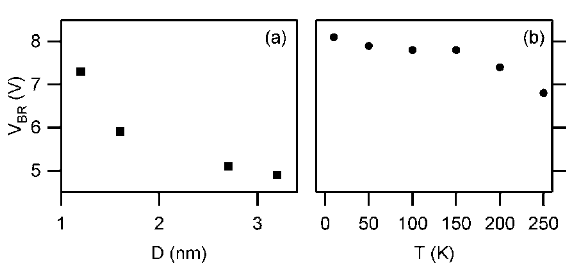

FIG. 5. Change of breakdown voltage with (a) nanotube diameter (200 K) and (b) temperature (1.6 nm diameter tube).

The second potential mechanism is avalanche breakdown. The electrons and holes in the intrinsic region accelerate in the electric field of the junction until they have enough energy to create a new electron-hole pair. Competing with this process is energy loss by phonon emission.[3,13–15] The spontaneous emission of large-energy ($\hbar\omega_0\sim 0.2$ eV) optic or band edge phonons occurs with a mean free path of $\ell\sim 30$ nm. In order for the energy gained by the electric field to exceed the energy lost by phonon emission, the voltage across the junction must be greater than

$$V_{br}(\text{avalanche}) > (\hbar\omega_0/e\ell)L = (8\ \text{V})(L[\mu\text{m}]). \qquad (5)$$

This estimate is consistent with the data, assuming a junction width L slightly smaller than the 1 μm distance between the gate electrodes. An increase of the breakdown voltage with tube diameter is also expected since the electron or hole must accelerate to a larger energy, but a specific prediction requires detailed knowledge of all the relevant scattering rates. Not all of the data are consistent with avalanche behavior, however. In most avalanche diodes, V_{br} increases as the temperature is raised, since raising the temperature increases phonon scattering. Further studies are therefore needed to unambiguously identify the breakdown mechanism.

In conclusion, we have shown that *p-i-n* nanotube diodes exhibit the behavior expected for a nearly ideal one-dimensional diode over a wide range of temperatures.

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