NANO LETTERS

2008
Vol. 8, No. 4
1253-1256

Effect of Negative Differential Conductance in Carbon Nanotubes

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Received November 21, 2007; Revised Manuscript Received February 14, 2008

ABSTRACT

Measurements of transport at high electric fields in metallic single-walled carbon nanotubes (CNTs) have shown either saturation of the current or a region of negative differential conductance (NDC) characterized by the current, after reaching a maximum, decreasing with further increase in voltage. We point out that both types of behavior are characteristic of NDC, but the NDC is masked in samples showing current saturation due to generation of space charge, leading to a nonuniform electric field. We derive the relation between the carrier concentration, the electric field at which the drift velocity peaks, and the length of the sample that is required for the NDC to be manifest as saturation.

The behavior of current (I) versus voltage (V) most usually observed in metallic carbon nanotubes (CNTs) at voltages as low as a few tenths of a volt, up to a volt, and beyond, is saturation, i.e., essentially constant I, or I increasing very slowly with increasing V.[1–5] Several of the authors who found saturation suggested that it results from the combination of acoustic mode scattering and scattering by higher energy phonons, optical or zone boundary.[1–5] The same suggestion had been made earlier to explain similar behavior, although at higher voltages, in three-dimensional semiconductors such as germanium.[6] As was well-known to those working on hot electrons in semiconductors in the 1950s and 1960s, solution of the Boltzmann equation does not bear this out.[6] The solution shows that for fields beyond the Ohm's law region, i.e., fields in which the electron "temperature" rises above the lattice temperature, scattering by acoustic phonons causes the mobility to decrease; subsequent introduction of scattering by higher energy phonons results in the steady-state distribution having fewer high-energy electrons, thus the mobility decreasing faster with increasing field, but current still increasing slowly with field rather than saturating.[6]

A situation that could lead to saturation, as will be discussed further, is the onset of negative differential conductance (NDC). NDC in semiconducting CNTs has been predicted to result from scattering that leads to electron transfer between the lowest subband and the next, in which the electrons have higher effective mass.[7] Electron transfer to a higher effective mass band was identified as the origin of NDC, leading to high-frequency oscillations called the Gunn effect, in GaAs and other semiconductors.[6] However, NDC due to electron transfer is not expected to apply to metallic CNTs, where there is no gap in the neighborhood of the Fermi energy.

A convincing demonstration of NDC of a different origin has been presented experimentally by Pop et al. for suspended metallic nanotubes.[8] As had been seen by others, they found that when V was increased beyond the Ohm's law region, I increased progressively more slowly as V increased. With suspended samples of length 0.8−11 μm, I was found to go through a maximum and then decrease with further increase in V.[8] Pop et al. were able to show that this NDC is due to a large excess of high-energy phonons over the thermal equilibrium value, thus "hot" phonons.[8,9] The hot phonons arise from phonon emission of electrons heated by the energy pumped into them by the high electric field. It should be remembered that heating of electrons is particularly effective in metallic CNTs, at least when the excess phonon population is not too large, because of the suppression of backscattering by long-range disorder.[10]

Note that it is not possible to have a hot phonon distribution without a hot electron distribution. (It would be possible to have a hot electron distribution with only a small increase in the number of phonons if the phonon lifetime were very short.) The energy of the phonons concerned is 0.16 eV if they are zone-boundary phonons, 0.2 eV if they are optical phonons. As pointed out by Yao et al.,[1] a requirement for an electron in a metallic CNT to emit such a phonon is that there be an empty state at an energy 0.16 or 0.2 eV below its energy. These phonon energies are many times kT at room temperature, thus many times the size of the tail on the Fermi−Dirac distribution, so it is necessary for the electrons to be hot in order for there to be sizable phonon emission. Further, at fields high enough for there to be a significant number of these high-energy phonons, interaction of the electrons with the phonons will contribute to keeping the electrons hot. If N_q is the number of phonons in this energy range with wavevector q, the ratio of emission

10.1021/nl073043n CCC: $40.75 © 2008 American Chemical Society
Published on Web 03/21/2008

to absorption of these phonons is $\sim(N_q + 1)/N_q$, which approaches unity in the high field limit.

Pop et al. found that the size of the peak current decreased as the length of the sample increased,[8] as expected because at a given field more phonons would be generated in longer samples. The latter could also explain the trend to the peak occurring at lower voltage in longer samples. For a length of 11 μm, the peak is so small that the current looks almost saturated. What was unexpected was that at greater lengths the suspended samples do not show peaks; they all show current saturation.[8]

To understand this phenomenon, it is necessary first to realize that in the presence of NDC unusual behavior of current versus voltage is expected for thermodynamic reasons.[11] In a sample with NDC, a departure from equilibrium such as a fluctuation of field or current will tend to grow rather than dissipate. Consider a small nonuniformity of the field at some point, due to either a momentary, or a permanent, deficiency of positive charge or accumulation of electrons such that the field upstream is higher than the field downstream. If the differential conductance of the sample is positive, a larger current will flow into the region than out, and the excess negative charge will be dissipated. If, however, the differential conductance is negative, more negative charge will accumulate and the original field discontinuity will be enhanced. These statements apply independent of sample dimensions and band structure. The effects of NDC have been seen and studied intensively in GaAs and related semiconductors,[6] and in n-Ge,[12] cases where, as mentioned earlier, it is due to electrons being scattered from one band, or region of k-space, to another where they have greater mass. It has also been shown, at least theoretically, that NDC can occur for the mass increase due to a nonparabolic band, without a gap being involved.[13]

Consider the case of a sample in which there is NDC over some range of fields, as is illustrated in Figure 1. In principle it is possible to obtain such a curve for a given material either theoretically or experimentally, as will be discussed below. In general, charge carrier density n and electric field intensity E can be expected to vary with position x inside a homogeneous medium as described by Poisson's equation

$$(\mathrm{d}E/\mathrm{d}x) = [n(x) - n_0]e/\varepsilon\varepsilon_0 \tag{1}$$

where n_0 is the thermal equilibrium carrier concentration and ε is the dielectric constant.

We neglect diffusion, which has only a small effect that is limited to the region near the electrodes. We neglect also possible loss of heat through the contacts, which would have some effect on the field near the contacts at currents where the phonon population is greatly increased. The current density j for a steady current may then be written

$$j = n(x)e\nu_d(E(x)) \tag{2}$$

where $\upsilon_d = \mu E$ is the drift velocity and μ the mobility. Eliminating $n(x)$ from eq 1 by the use of eq 2, we obtain

$$(\mathrm{d}E/\mathrm{d}x) = (en_0/\varepsilon\varepsilon_0)[(j/en_0\nu_d(E(x)) - 1] \tag{3}$$

NDC results from the variation of μ with E, specifically μ decreasing with increasing E more so than $1/E$. In low fields

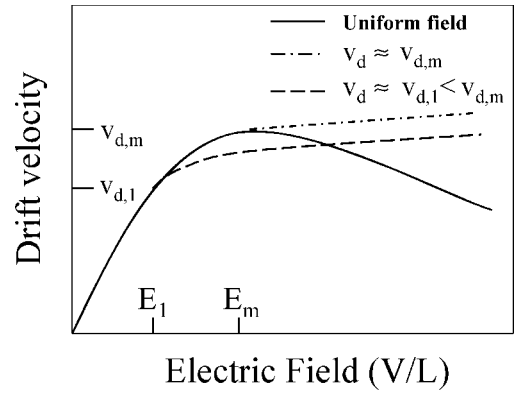

Figure 1. Plots of j/n_0e vs E for sample with NDC.

the electron temperature T_e is only slightly larger than the lattice temperature to slightly increase phonon emission (Joule heating) over absorption, μ is constant and υ_d increases linearly with E. At fields high enough to perceptibly increase T_e, when phonon scattering is dominant μ decreases, the more so the larger the field. If there is NDC but the field remains uniform (we assume nonuniformity in phonon temperature can be neglected), υ_d reaches a maximum $\upsilon_{d,m}$ at a field E_m, and decreases with further increase in E over the range in which the NDC persists, as is illustrated in Figure 1.

Let us apply this to the case of a sample of length L with thin heavily doped (ohmic) contacts at both ends. Also, we assume that the fractional decrease in the current due to NDC is not large; it is no more than $\sim$25% for the samples shown by Pop et al. in their Figure 3.[8] We consider how the current behaves for two different values of υ_d, the first $\upsilon_d = \upsilon_{d,1}$, below $\upsilon_{d,m}$ but in the range where there are two values of E corresponding to a given υ_d. At the cathode, $x = 0$, $\mathrm{d}E/\mathrm{d}x$ diverges because of the choice of heavily doped contacts. However, it becomes finite for $x > 0$ and decreases with increasing x such that, at some field E_1, $\upsilon_d = \upsilon_{d,1}$. Denoting as x_1 the distance required to attain the value E_1, we find that the angular bracket in eq 3 vanishes for $x = x_1$ and beyond this region the field remains constant at E_1.[12,14] From eq 1 we can deduce that the distance $x_1 \approx \varepsilon\varepsilon_0E_1/n_0e$. For weak NDC E_1 cannot be much less than E_m. Thus, if $(\varepsilon\varepsilon_0E_m/e) \ll n_0L$, the distance taken for the field to build up to the value E_1 is small compared to L. Most of the sample then has a constant field of $E_1 \approx E_m$ and the current density saturates at $\sim n_0e\ \upsilon_{d,1}$. This behavior is shown in Figure 1.

Consider now the behavior of eq 3 for a second value of υ_d, slightly larger than $\upsilon_{d,m}$. For this value of υ_d, j is greater than $n_0e\upsilon_d(E_m)$ and $\mathrm{d}E/\mathrm{d}x$ is always positive. There is an inflection point in E at the maximum field E_m, and beyond this field E rises rapidly with increasing x, resulting in a high field domain.[12,14] To obtain a relation between the length of the sample L and the other quantities in (3) we now integrate eq 3 from $x = 0$ to L, replacing the field at the cathode by E_m as the lower limit to avoid the divergence at the cathode. The result, for not too strong NDC, is[12]

$$(\varepsilon\varepsilon_0E_m/e) \cong n_0L[(j/en_0\nu_d(E_m)) - 1] \tag{4}$$

We see that in the limit $n_0L \gg \varepsilon\varepsilon_0E_m/e$ the quantity in brackets must be small to satisfy eq 4. Thus in this limit j

has a value close to $n_0 e v_d(E_m)$; i.e., the current saturates, as shown in Figure 1. Incorporating the results obtained above for the case where $v_d < v_{d,m}$, although in the range where the same value of v_d is seen for two different fields, we conclude that current saturation is seen at high voltages for any v_d in this range provided $n_o L \gg \varepsilon\varepsilon_0 E_m/e$.

We note that the finding of a low field region at the cathode and a high field region at the anode results from the boundary conditions we have chosen of low resistance contacts at both ends of the sample. If the heating of the sample were uniform, in the presence of a high resistance contact at the cathode the high field region would be at the cathode. However, the heating of the sample is likely to be nonuniform, as pointed out in ref 15. For a nonuniform sample, the high field region could be elsewhere in the sample. For a discussion of the effect of boundary conditions see refs 11 or 16.

From the above discussion it is clear that the reason the decrease in I with increasing V is seen in some of the samples of Pop et al.[8] is that the thermal equilibrium carrier concentration in those samples is not sufficient to build up the space charge required to generate the nonuniform field in the distance L. In the absence of space charge layers the $I-V$ characteristic is what would be seen in a uniform field. It is a reasonable guess that some space charge will have built up even in the samples that display NDC rather than saturation, so that the I vs V curve differs from the I vs V that would be seen for a really uniform field. It is clear that the nonequilibrium optical phonon concentration is larger in the longer samples shown in Figure 3 of ref 8 because for the longer samples I is greatly decreased at the same voltage and the NDC starts at lower voltages.

In the experiments of Javey et al.[2] and Park et al.[3] on nonsuspended CNTs, current saturation was observed for samples of length 300 nm and longer. Pop et al. also found that a nonsuspended sample 3 μm in length was very close to saturation at 1.2 V. (See Figure 2 of ref 8.) These observations suggest that the surmise of Pop et al.[8] that NDC due to hot phonons exists at high fields in nonsuspended CNTs as well as suspended ones is correct. For CNTs of length 100 nm up to 300 nm I vs V of the samples of refs 2 and 3 show what might be called "almost saturation", coming closer to saturation as the length increases. We suggest that NDC occurs also for these samples.

Another phenomenon that has been seen in CNTs is the degree of saturation varying somewhat erratically between samples. In the data of Javey et al., current in the saturation range is increasing a little more steeply with increasing field for a 700 nm sample than for a 300 nm sample, contrary to expectations. This type of effect was found also for n-Ge samples, for example, in the NDC range.[12] It was noted there that in this range small nonuniformities in a sample produce gross nonuniformities in the electric field distribution. This is not unexpected from the description of NDC given earlier. Inhomogeneity might also account for the observation of a slight NDC in the saturated current seen in some CNT-samples.

To characterize the NDC at a more fundamental level, it is preferable to describe it in terms of v_d vs E as shown in the unbroken line in Figure 1 rather than in terms of I vs V. In principle it is possible to ascertain v_d vs E in a uniform field by carrying out the measurements in a time so short that the space charge has not yet developed. This time is less than a nanosecond for GaAs in the NDC region but long enough for the measurement without space charge to be carried out.[17] For the CNTs it may not be possible to make measurements at a time when the optical phonon distribution has reached a steady state but the space charge has not yet developed. Theoretical calculations are of course possible. They will require setting up and solving coupled equations for the hot electrons and hot phonons. This was partially done by Kuroda and Leburton,[15] who also took into account an inhomogeneous optical phonon distribution but did not allow for a nonuniform voltage distribution. Also it is not clear that they accounted properly for hot electrons.

It is of interest to inquire what n_0 must be for a given L to satisfy the condition derived above for saturation of the current. We take as an example the sample of length 0.8 μm in ref 8. For this sample the voltage for maximum current, according to Figure 3 of ref 8 is 0.7 V, corresponding to $E \approx 10^4$ V/cm if the field were uniform. We speculated earlier that there is probably some space-charge buildup in this sample at this voltage, but the maximum field is probably not too different from 10^4 V/cm. Taking $\varepsilon = 4.5$, we find n_0 required to equal $\varepsilon\varepsilon_0 E_m/eL$ is $10^{14}/\text{cm}^3$. It is undoubtedly possible to get larger carrier concentrations than this, whether through judicious choice of the parameters m,n of the nanotube, or doping with impurities.

In summary, the current saturation seen at high fields in CNTs originates in NDC stemming from hot electrons. This is true for current saturation in 3d semiconductors as well as the 1d nanotubes, although in detail it is the transferred electron effect in the former vs a hot phonon distribution in the latter that is responsible for the NDC. Mobility values at high fields deduced by many workers characterizing CNTs may not be meaningful because they have not taken into account the nonuniform electric field resulting from the NDC. We have demonstrated that for the current to show saturation or near saturation at fields for which NDC exists requires that the CNT satisfy the condition $n_0 L > \varepsilon\varepsilon_0 E_m/e$.

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NL073043N