Negative Differential Conductance and Hot Phonons in Suspended Nanotube Molecular Wires

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Freely suspended metallic single-walled carbon nanotubes (SWNTs) exhibit reduced current carrying ability compared to those lying on substrates, and striking negative differential conductance at low electric fields. Theoretical analysis reveals significant self-heating effects including electron scattering by hot nonequilibrium optical phonons. Electron transport characteristics under strong self-heating are exploited for the first time to probe the thermal conductivity of individual SWNTs (~ 3600 W m^{-1} K^{-1} at $T = 300$ K) up to ~ 700 K, and reveal a $1/T$ dependence expected for umklapp phonon scattering at high temperatures.

The current carrying ability of materials is fundamental and important to a wide range of applications from power transmission to high performance electronics. It is now well established that when in contact with a substrate, metallic single-wall carbon nanotubes (SWNTs) can carry tens of microamperes of current [1,2]. Nevertheless, little is known about the high bias transport properties of suspended SWNTs in native unperturbed states. In general, high-field transport in quasi-one-dimensional (1D) materials is significantly affected by the surrounding environment due to reduced dimensionality for thermal conduction and phonon relaxation. These are also important to high power applications of 1D materials including nanotubes and nanowires, and neither has been carefully explored.

Here, we uncover that suspended SWNTs display drastically different electron transport and phonon scattering than SWNTs on substrates. Experimentally, suspended SWNTs with Pt electrical contacts were obtained by direct growth across preformed trenches of widths 0.6–10 μm (Fig. 1), as described previously [3,4]. Devices comprised of an individual nanotube with a nonsuspended (lying on silicon nitride) and a suspended segment over a trench were also fabricated [Figs. 1(a) and 1(b)] for comparison. The devices were characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM) to obtain nanotube diameter (d) and length (L) information. We note that the obtained suspended SWNTs are typically longer than the trench width as most tubes form across the gap at a slight angle. All electrical measurements were carried out in *vacuum* at *room temperature* (RT) ($T_0 \sim 300$ K).

The same-length suspended and nonsuspended portions of a metallic SWNT ($d \sim 2.4$ nm, $L \sim 3$ μm, Fig. 2) exhibit drastically different current vs voltage (I-V) characteristics at high bias [Fig. 2(a)]. The nonsuspended SWNT portion shows monotonic I-V with I approaching ~ 20 μA under increasing V, while the current in the suspended tube reaches a peak of $I_{\text{peak}} \sim 5$ μA followed by a pronounced negative differential conductance (NDC) region [Fig. 2(a)]. We find that current peaking and NDC are universal char-

acteristics of all suspended SWNTs in the range $L = 0.8$–11 μm [Fig. 3(a)]. A systematic decrease in I_{peak} is seen for longer suspended tubes with $I_{\text{peak}} \sim 10$ μA/L (with L in μm) measured across many suspended tubes [Fig. 3(b)]. We note that we have found no hysteretic behavior, and the I-V characteristics (with NDC) are reproducible with each repeated voltage sweep from low to high and high to low.

The NDC behavior of freely suspended SWNTs starting at electric fields as low as 200 V/cm (for $L \sim 10$ μm tubes) cannot be explained by the velocity saturation expected theoretically at much higher fields (~ 5 kV/cm) under isothermal conditions [5,6]. Isothermal conditions (i.e., no appreciable self-heating) are typically assumed for electron transport in SWNTs on substrates due to heat sinking by the substrate [1–7]. The I-V curve can be calculated by $I = V/R(V)$ with resistance $R(V) = R_c + (h/4q^2)[L + \lambda_{\text{eff}}^{\text{RT}}(V)]/\lambda_{\text{eff}}^{\text{RT}}(V)$ where R_c is the contact resistance. The RT total electron scattering mean free path (MFP) [8] is $\lambda_{\text{eff}}^{\text{RT}}(V) = [1/\lambda_{\text{ac}}^{\text{RT}} + 1/\lambda_{\text{op,em}}^{\text{RT}}(V)]^{-1}$ with acoustic phonon (ac) scattering MFP [9,10] $\lambda_{\text{ac}}^{\text{RT}} \sim 1600$ nm and optical phonon (op) emission MFP $\lambda_{\text{op,em}}^{\text{RT}}(V) = \hbar\omega_{\text{op}}L/qV + \lambda_{\text{op,min}}$ [7], where the first term (q = electron charge) represents the distance required by electrons to reach the op emission threshold [1] energy $\hbar\omega_{\text{op}} \sim 0.18$ V and $\lambda_{\text{op,min}} \sim 15$ nm [1,9] is the MFP of op emission after reaching the threshold. At RT, scattering by op absorption can be neglected due to the large energy of optical phonons in SWNTs ($\hbar\omega_{\text{op}} \gg k_B T$) and their low population. The I-V characteristic thus calculated fits well the experimental data of the SWNT on substrate for $V < 1$ V [Fig. 2(a)]. This model overestimates currents for $V > 1$ V [Fig. 2(a)], indicating that the isothermal condition may not hold at higher biases under which self-heating starts to manifest itself in the $L \sim 3$ μm SWNT on substrate.

For suspended SWNTs in vacuum, when heat dissipation only occurs along the tube length to the contacts (1D thermal transport), we consider self-heating and a bias-

dependent temperature profile of the nanotube. The *I-V* characteristics are calculated by $I = V/R(V, T)$, where $R(V, T) = R_c + (h/4q^2)[L + \lambda_{\text{eff}}(V, T)]/\lambda_{\text{eff}}(V, T)$ and $\lambda_{\text{eff}}(V,T) = [1/\lambda_{\text{ac}}(T) + 1/\lambda_{\text{op,ems}}(V, T) + 1/\lambda_{\text{op,abs}}(V, T)]^{-1}$ are *V* and in turn *T* dependent. The ac scattering MFP scales as $\lambda_{\text{ac}}(T) = \lambda_{\text{ac}}^{\text{RT}}(300 \text{ K}/T)$ since acoustic phonons are thermally occupied with energies $\hbar\omega_{\text{ac}} \ll k_B T$ at RT and above [7]. The op emission and absorption MFP are $\lambda_{\text{op,ems}}(T) = \hbar\omega_{\text{op}}L/qV + \lambda_{\text{op,min}}[N_{\text{op}}(300 \text{ K}) + 1]/[N_{\text{op}}(T) + 1]$ and $\lambda_{\text{op,abs}}(T) = \lambda_{\text{op,min}}[N_{\text{op}}(300 \text{ K}) + 1]/N_{\text{op}}(T)$, respectively, with $N_{\text{op}} = 1/[\exp(\hbar\omega_{\text{op}}/k_B T) - 1]$ as the op occupation number. In the limit of $N_{\text{op}} \sim 0$
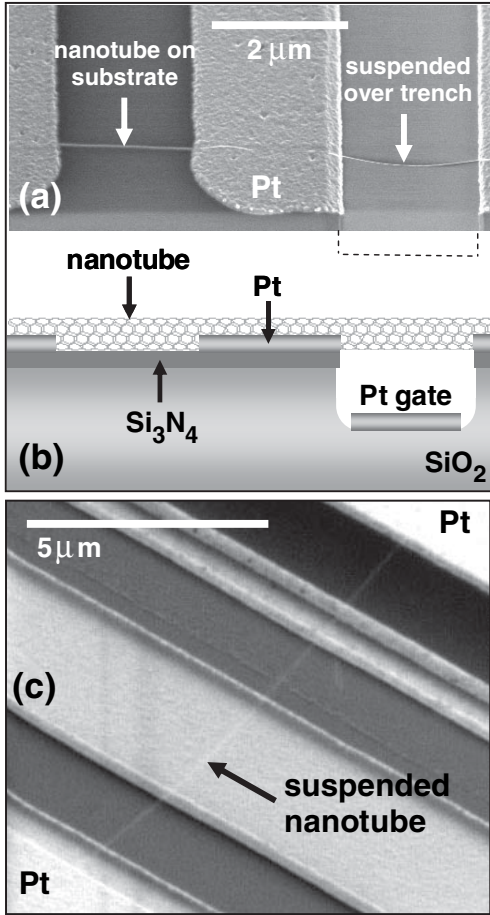

FIG. 1.   Freely suspended nanotube devices. (a) SEM image, taken at a 45° angle, of the nonsuspended (on nitride) and suspended (over a ~ 0.5 μm deep trench, entirety of trench depth not shown in the image) $L \sim 2$ μm nanotube segments of an individual nanotube, both segments with Pt contacts under the tube [3,4]. (b) A schematic of the device cross section. (c) SEM image of a nanotube suspended over a trench across a ~ 10 μm Pt electrode gap. The bright features between the Pt electrodes were metal lines at the bottom of the wide trench used as local gates. The diameters of the nanotubes were measured by AFM in the range of $d \sim 2$–3 nm. Nanotubes grown under the same condition on transmission electron microscope (TEM) grids were confirmed to be single-walled by TEM.

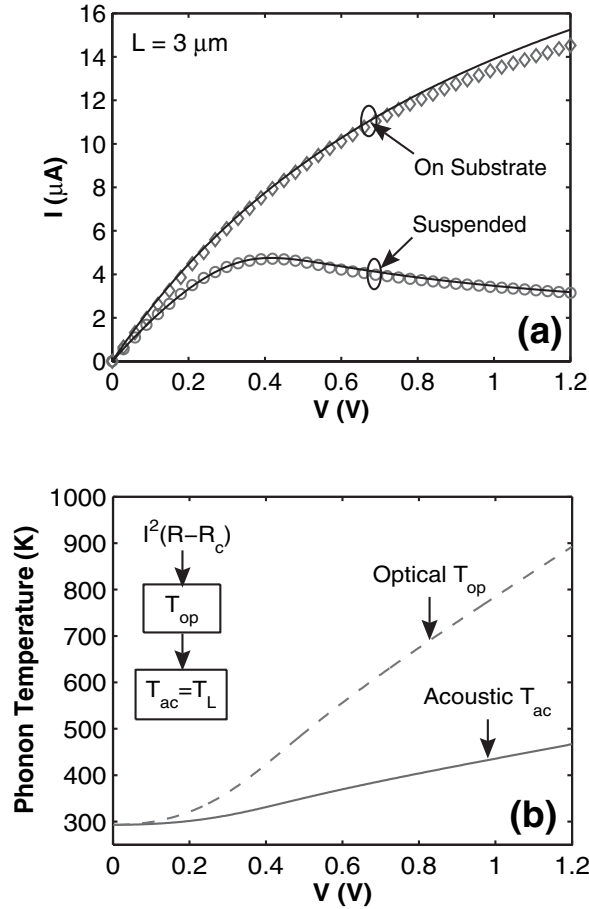(below or near RT for $\hbar\omega_{\text{op}} \gg k_B T$) this model gives a long op absorption MFP, $\lambda_{\text{op,abs}}(T)$, as expected.

At a given bias *V* the lattice temperature of the suspended SWNT is determined by the power dissipation $P = I^2(R - R_c)$ and the thermal conductivity $\kappa(T)$ of the tube. The average temperature along the tube is $T = T_0 + I^2(R - R_c)L/(12\kappa(T)A)$ where $T_0 \sim 300$ K is the electrode (contact) temperature, $A = \pi db$ is the cross-sectional area and $b = 0.34$ nm is the tube wall thickness. The average tube temperature is used to compute the various MFPs, then $R(V, T)$ and the *I-V* characteristics. The SWNT thermal conductivity is expected to follow $\kappa(T) = \kappa_0(T_0/T)$ at high temperatures due to umklapp phonon-phonon scattering [11,12] where κ_0 is the RT thermal conductivity. Since $R(V, T)$ and $I(V)$ depend on *T*, which is in turn dependent on *I* and $\kappa(T)$, we use an overdamped iterative approach to compute the *I-V* characteristics until *T* converges within 0.1 K for each bias *V*.

If the op population is assumed in equilibrium with the lattice (ac phonon) temperature, the model (with $\kappa_0 \sim 1800$ W m^{-1} K^{-1}) can reproduce the *I-V* curve of the $L \sim 3$ μm suspended SWNT only at a staggeringly high peak lattice temperature of $T > 1500$ K at $V \sim 1.5$ V. This is contradicted by the fact that suspended SWNTs under such bias were never oxidized or lost connection upon exposure to air or a partial pressure of oxygen (the onset of oxidation is known to occur around $T \sim 800$ K [13]) until $V > 2$–2.5 V. Without the nanotube at exceedingly high lattice temperature, a rational mechanism for the low current and NDC characteristic of suspended SWNTs is the existence of nonequilibrium, hot op's at high bias. Since only few of the numerous optical branches of a SWNT are involved in scattering electrons [6] their density of states is relatively small. Their population will quickly build up in a suspended tube if the emitted op's cannot immediately decay into other (lower energy or electrically inactive) modes [Fig. 2(b) inset] or into the contacts. This is consistent with the over-population of the radial breathing mode of suspended SWNTs observed in recent low temperature tunneling experiments [14] and with narrower Raman phonon linewidths for suspended SWNTs [15]. Recent theory has also suggested nonequilibrium optical phonons may exist under high biases in SWNTs on substrates [16].

We model the nonequilibrium optical phonons with an effective temperature $T_{\text{op}}^{\text{eff}} = T_{\text{ac}} + \alpha(T_{\text{ac}} - T_0)$. This linear relation can be written since Joule power is primarily dissipated to the op modes (which is the case for high bias transport in SWNTs) and then decays into ac modes [Fig. 2(b) inset] and to the environment (T_0). This is similar to previous approaches that have been used for treating nonequilibrium phonons in GaAs and Ge [17–19]. The nonequilibrium coefficient $\alpha > 0$ can be interpreted as the ratio of the thermal resistance of op-ac decay to that of ac conduction along the tube, to the contacts at T_0. The *I-V* curves are then calculated as $I = V/R(V, T_{\text{op}}^{\text{eff}}, T_{\text{ac}})$.

FIG. 2.   High-field electron transport in suspended nanotubes.
(a) Current-voltage (*I-V*) characteristics of the same-length (*L* ∼
3 μm) suspended and nonsuspended portions of a SWNT (*d* ∼
2.4 nm) at room temperature measured in vacuum. The symbols
represent experimental data; the lines are calculations based on
average tube temperature (similar within ∼5% to that based on
actual tube temperature profile and resistance integrated over the
∼3 μm tube length). (b) Computed average acoustic (lattice)
and effective optical phonon temperature vs bias voltage for the
suspended tube segment in (a) quantifying the degree of self-
heating. The figure inset shows the energy flow in our model
from electrons ("heated" by the electric field) to optical phonons
and then acoustic phonons. We estimated the heat dissipation by
radiation (ignored in our model) to be less than 1% of the power
input even up to average SWNT temperatures $T \sim 800$ K.
Dissipation at the contacts ($I^2 R_c$) is estimated to be less than
5% at high bias.

We found that with $\kappa(T_{ac}) = \kappa_0(T_0/T_{ac})$ where the RT
thermal conductivity $\kappa_0 \sim 3600$ W m^{-1} K^{-1} (in line with
that of multiwalled nanotubes [20]) and $\alpha = 2.4$, our
model reproduced the experimental *I-V* curves including
NDC remarkably well over a wide range of suspended
SWNT lengths and biases [21] [Figs. 2(a) and 3(a)]. The
self-heating (T_{op}^{eff} and T_{ac}) of the suspended SWNTs was
also calculated at various biases [Fig. 2(b)]. Importantly,
the $I \sim I/V$ shape of the *I-V* curves in the NDC region is

found to strongly reflect the temperature dependence of the
thermal conductivity $\kappa(T) \sim 1/T$ that results from um-
klapp phonon scattering at RT and above [11,12] (electron
contribution negligible [22]). Alternative models for the *T*
dependence of the thermal conductivity (e.g., $\kappa(T) \sim$
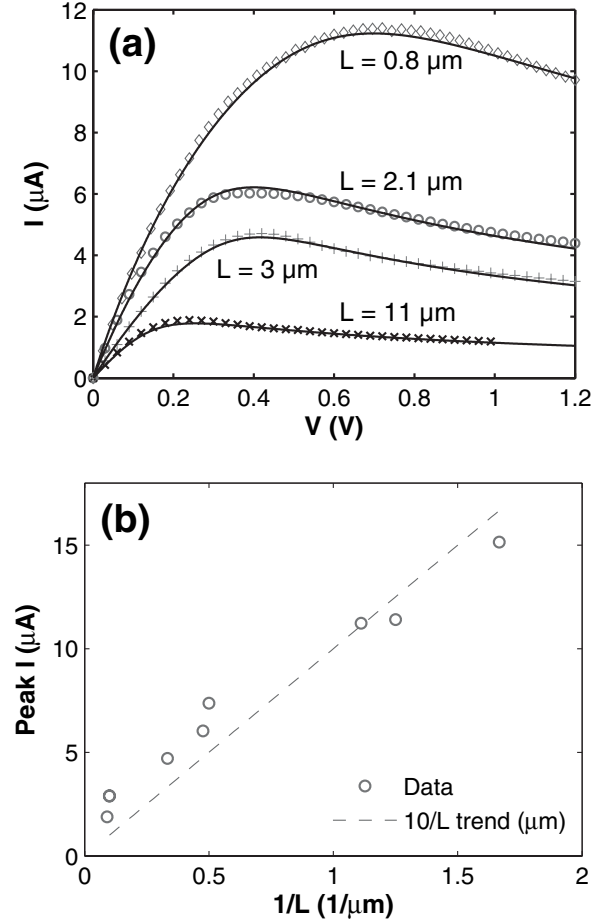constant, or $\kappa(T) \sim$ linearly decreasing in *T*) cannot repro-

FIG. 3.   Currents in various-length suspended SWNTs. (a) *I-V*
of four suspended tubes with lengths: $L \sim 0.8$, 2.1, 3, and
11 μm. Symbols are experimental data; solid lines are calcu-
lations. The *I-V* curves are highly reproducible over many
sweeps without irreversible changes to the device, indicating
that the electrical characteristics are not due to irreversible
contact change. The tube diameters used in the calculation
(consistent with AFM) were $d \sim 2$, 2.4, 2.4, and 3.2 nm, respec-
tively. The contact resistance R_c was used as a parameter to fit
the *I-V* curves at low bias. $R_c \sim 15$ kΩ for all tubes except for
$L = 3$ μm which had $R_c \sim 30$ kΩ. This contact resistance is
much lower than the resistance along the tube under high bias
and most (> 95 percent) of the power dissipation occurs along
the tube length rather than at the contacts. (b) Measured peak
current (symbols) for suspended SWNTs of various lengths. The
peak current scales approximately as $\sim 1/L$ just like the thermal
conductance of the suspended nanotubes, an additional indicator
that this is a thermally limited effect. The deviation from the $1/L$
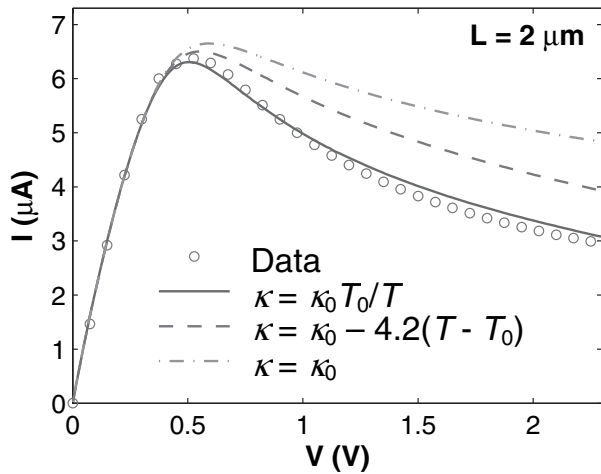behavior is attributed to variations in diameter between the
different tubes.

FIG. 4. Electrical characteristics of a 2 μm suspended tube in vacuum (experimental data with symbols) and calculations (lines) based on three different thermal conductivity models with $\kappa_0 = 3600$ W m^{-1} K^{-1} at $T_0 = 300$ K. The high bias region of the *I-V* curve provides an indirect measurement of the temperature dependence of the thermal conductivity for 400 K $< T < 700$ K. Here, as in the rest of our Letter, T refers to the lattice (ac phonon) temperature.

duce the *I-V* characteristics of suspended SWNTs (Fig. 4 dashed lines). Thus, we show that self-heating and *I-V* measurements on suspended SWNTs can be exploited to probe their thermal conductivity from RT up to $\sim$700 K (V up to $\sim$2.2 V).

Our study suggests that SWNTs suspended in vacuum, by virtue of their free unperturbed state, present the extreme scenario of longest op lifetime and hence the strongest nonequilibrium op population at high bias. The higher currents observed in nanotubes on substrates are owed to the substrate-tube interaction that aids heat dissipation and more importantly assists the relaxation of op's emitted through electron scattering. Self-heating and hot phonons are also thought to exist in nanotubes lying on substrates [16], although at higher biases [> 1 V in Fig. 2(a)] and electric fields than in suspended tubes. This raises the interesting possibility that SWNTs on substrates may be engineered to deliver higher currents than previously thought possible (for a given tube length) through rational interface design for optimized heat dissipation and op

relaxation. This scenario is of considerable consequence for electronics and may have general implications for high-current applications of quasi-1D materials. The effects uncovered here could also be exploited for new device applications of suspended SWNTs.

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