Direct pressure sensing with carbon nanotubes grown in a micro-cavity

A. S. Chauhan and A. Nogaret

Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom

(Received 30 October 2012; accepted 31 May 2013; published online 12 June 2013)

We report on the growth of multiwall carbon nanotubes (CNTs) at the centre of a bow tie micro-cavity and describe the change in resistance of these CNTs under gas pressure loading (ΔR/R ≥ 16%/atm). By adapting the Euler-Bernoulli theory of beams to CNTs that bridge opposite walls of the cavity, we fit the piezoresistance curves and extract the Young’s modulus, the piezoresistive constant, and the nanotube radius, for a range of CNT growth conditions. By detecting pressures as low as 0.1 atm, we demonstrate a membrane-less technology capable of sensing pressure with micron scale resolution.

The electromechanical properties of carbon nanotubes (CNTs) are the focus of intense interest both in experiments and in devices that use the piezoresistance of CNTs for sensing pressure. Cao et al. have reported the highest piezoresistance to date in quasi-metallic single wall CNTs subjected to either tensile or compressive stress. The piezoresistance of multiwall CNTs is known to arise from the telescopic sliding of CNT shells which increases the CNT resistance when the wall-to-wall distance decreases. By adapting the E uler-Bernoulli theory of beams to CNTs that bridge opposite walls of the cavity, we fit the piezoresistance curves and extract the Young’s modulus, the piezoresistive constant, and the nanotube radius, for a range of CNT growth conditions. By detecting pressures as low as 0.1 atm, we demonstrate a membrane-less technology capable of sensing pressure with micron scale resolution.

The cavi- et al. nes were used to deposit Ni over an area of 50 μm × 50 μm centred on the constriction. The Ni film was evaporated over the top slab after its SiO2 layer had been stripped off by hydrofluoric acid etch. 150 nm thick Au contacts were then fabricated on the back surfaces of the top and bottom slabs. The top slab was flipped over the bottom slab to form the micro-cavity (Figures 1(b) and 1(c)). The two slabs were sealed together using sodium silicate (Na2SiO3·H2O) cured at 750 °C. Curing also allowed the Ni film to coalesce into a thin film that covered the entire surface of the micro-cavity. The CNTs were then grown on the Ni film using chemical vapour deposition (CVD) of CH4 until they anchor themselves to the opposite walls of the cavity. We monitor this process by detecting the change in resistance during CVD growth. We study the piezoresistance of CNTs prepared under different growth conditions: temperature, time, and methane flow rate. The piezoresistance is found to be as high as 16% at 1 atm compared to 3.5%/atm for GaAs membranes.

We show that the change in resistance with pressure is well described by Euler-Bernoulli theory modeling CNTs as elastic beams which are free to pivot at anchor points. A fit of the experimental piezoresistance curves with this theory yields the Young modulus of CNTs, the piezoresistive constant, and the average radius of the CNTs which we find to be in good agreement with either the published values or the CNT dimensions on electron microscope images.

The cavi- et al. nes were used to deposit Ni over an area of 50 μm × 50 μm centred on the constriction. The Ni film was evaporated over the top slab after its SiO2 layer had been stripped off by hydrofluoric acid etch. 150 nm thick Au contacts were then fabricated on the back surfaces of the top and bottom slabs. The top slab was flipped over the bottom slab to form the micro-cavity (Figures 1(b) and 1(c)). The two slabs were sealed together using sodium silicate (Na2SiO3·H2O) cured at 750 °C. Curing also allowed the Ni film to coalesce into a thin film that covered the entire surface of the micro-cavity. The CNTs were then grown on the Ni film using chemical vapour deposition (CVD) of CH4 until they anchor themselves to the opposite walls of the cavity. We monitor this process by detecting the change in resistance during CVD growth. We study the piezoresistance of CNTs prepared under different growth conditions: temperature, time, and methane flow rate. The piezoresistance is found to be as high as 16% at 1 atm compared to 3.5%/atm for GaAs membranes.

We show that the change in resistance with pressure is well described by Euler-Bernoulli theory modeling CNTs as elastic beams which are free to pivot at anchor points. A fit of the experimental piezoresistance curves with this theory yields the Young modulus of CNTs, the piezoresistive constant, and the average radius of the CNTs which we find to be in good agreement with either the published values or the CNT dimensions on electron microscope images.

The cavi- et al. nes were used to deposit Ni over an area of 50 μm × 50 μm centred on the constriction. The Ni film was evaporated over the top slab after its SiO2 layer had been stripped off by hydrofluoric acid etch. 150 nm thick Au contacts were then fabricated on the back surfaces of the top and bottom slabs. The top slab was flipped over the bottom slab to form the micro-cavity (Figures 1(b) and 1(c)). The two slabs were sealed together using sodium silicate (Na2SiO3·H2O) cured at 750 °C. Curing also allowed the Ni film to coalesce into a thin film that covered the entire surface of the micro-cavity. The CNTs were then grown on the Ni film using chemical vapour deposition (CVD) of CH4 until they anchor themselves to the opposite walls of the cavity. We monitor this process by detecting the change in resistance during CVD growth. We study the piezoresistance of CNTs prepared under different growth conditions: temperature, time, and methane flow rate. The piezoresistance is found to be as high as 16% at 1 atm compared to 3.5%/atm for GaAs membranes.

We show that the change in resistance with pressure is well described by Euler-Bernoulli theory modeling CNTs as elastic beams which are free to pivot at anchor points. A fit of the experimental piezoresistance curves with this theory yields the Young modulus of CNTs, the piezoresistive constant, and the average radius of the CNTs which we find to be in good agreement with either the published values or the CNT dimensions on electron microscope images.

The cavi- et al. nes were used to deposit Ni over an area of 50 μm × 50 μm centred on the constriction. The Ni film was evaporated over the top slab after its SiO2 layer had been stripped off by hydrofluoric acid etch. 150 nm thick Au contacts were then fabricated on the back surfaces of the top and bottom slabs. The top slab was flipped over the bottom slab to form the micro-cavity (Figures 1(b) and 1(c)). The two slabs were sealed together using sodium silicate (Na2SiO3·H2O) cured at 750 °C. Curing also allowed the Ni film to coalesce into a thin film that covered the entire surface of the micro-cavity. The CNTs were then grown on the Ni film using chemical vapour deposition (CVD) of CH4 until they anchor themselves to the opposite walls of the cavity. We monitor this process by detecting the change in resistance during CVD growth. We study the piezoresistance of CNTs prepared under different growth conditions: temperature, time, and methane flow rate. The piezoresistance is found to be as high as 16% at 1 atm compared to 3.5%/atm for GaAs membranes.

We show that the change in resistance with pressure is well described by Euler-Bernoulli theory modeling CNTs as elastic beams which are free to pivot at anchor points. A fit of the experimental piezoresistance curves with this theory yields the Young modulus of CNTs, the piezoresistive constant, and the average radius of the CNTs which we find to be in good agreement with either the published values or the CNT dimensions on electron microscope images.
CNTs grown at 875°C reach a concentration of CNTs increases dramatically once growth starts dropping 6 min after the admission of CH₄ which signals the onset of conduction through CNTs (Figures 2(b)–2(d)). The accepted CNT growth rate (1200 nm/min) suggests that CNTs bridge the 2.3 μm gap in 2 min. The 4 extra minutes prior to the resistance drop may be required for CNT endings to migrate on the opposite surface until they attach to a Ni island. Another possibility is that the diffusion rate of methane is lower in the confined space of the cavity. We have grown CNTs over 8, 9, 10, 11, and 12 min, in methane flow rates of 40 sccm and 60 sccm and at temperatures of 800°C, 850°C, 875°C, and 900°C to obtain various CNT densities and CNT radii. SEM micrographs show that CNTs tend to grow with random orientations (Figure 2(d)).

The growth temperature is the main parameter controlling CNT growth. At temperatures below 850°C, CNT growth is sparse (Figure 3(a)). This is confirmed by X-ray energy dispersive spectra (X-EDS) that show residual traces of carbon in the cavity at 800°C and 850°C (Figure 3(a)). The concentration of CNTs increases dramatically once growth temperature reaches 875°C. The CNT radius is at ≈12 nm at 800°C–875°C, rising to at ≈25 nm at 900°C. Now turning up to the I-V curves measured across the cavity (Figure 3(b)), CNTs grown at 875°C and 900°C are quasi metallic. Their I-V curves remain Ohmic down to 77 K (Figure 3(c)). The current follows a thermionic activation law characterized by a work function of 12 meV. This behavior is consistent with multi-wall CNTs incorporating structural defects. The resistance of the device prepared at 875°C corresponds to 10–12 CNTs bridging the cavity. In contrast, CNTs grown at lower temperature (800°C, 850°C) are semiconductors. Figure 3(c) shows that their zero bias conductance vanishes at 77 K. We have verified that CNTs require anchoring to Ni islands on opposite walls of the cavity in order to conduct. CNTs grown in a cavity having Ni islands on one wall only led to an increase in cavity resistance by a factor of 10⁵. Furthermore, X-EDS spectra taken in the Si and SiO₂ areas of slabs revealed no carbon residues susceptible of giving current leakage.

Next, we inserted the sensor in the hermetically sealed enclosure of Figure 1(d) to monitor the resistance of the cavity as a function of the pressure of N₂ gas applied across it. The CNTs remained in N₂ atmosphere throughout to avoid changes in resistance induced by oxidation. We focused on cavities with multiwall CNTs grown at 875°C. Pressure is found to increase the cavity resistance (Figure 4) as multiwall CNTs are put under tensile strain. Initially, the piezoresistance ΔR/R increases quadratically then saturates.

To explain the pressure response, we construct a theory assimilating CNTs to elastic nano-beams characterized by their Young’s modulus E and length L. We further assume that the modelled CNTs grow perpendicular to the top and bottom slabs (x-axis) and that the anchor points apply no bending moment to their extremities. The piezoresistance is given by

\[ \frac{\Delta R}{R} = \pi_L E \frac{\Delta L}{L}, \]

where \( \pi_L \) is the piezoresistive constant and \( \Delta L/L \) is the axial strain due to gas pressure \( \Delta P = P_{IN} - P_{OUT} \). The force applied per unit length of the nanotube is \( q = 2a\Delta P \), where \( a \) is the...
CNT radius. We compute the axial strain by solving the Euler-Bernoulli equation

$$\frac{d^2M}{dx^2} + \frac{T_s}{EI} M = -q,$$  
(2)

using $M(\pm L/2) = 0$ for the boundary conditions on the bending moment at each end of the CNT. $I = \pi a^4/4$ is the second moment of inertia of the nanotube and $T_s$ is the tension normal to the interface at anchor points. The bending moment relates to the transverse deflection of the beam $y(x)$ through

$$M = -EI \frac{d^2y}{dx^2}.$$  
(3)

Integrating Eqs. (2) and (3) with boundary conditions $y(\pm L/2) = 0$ gives the slope of the beam

$$\frac{dy}{dx} = -\frac{q}{T_s} \frac{1}{K} \sin(kx) \cos(kL/2) - x,$$  
(4)

where $k = \sqrt{T_s/EI}$ is the deformation wavevector. The strain in the CNT then follows as

$$\frac{\Delta L}{L} = \frac{1}{L} \int_{-L/2}^{+L/2} dx \left( \sqrt{1 + \left( \frac{dy}{dx} \right)^2} - 1 \right).$$  
(5)

Inserting Eq. (5) into Eq. (1) gives the piezoresistance which is the equation we seek to model the pressure dependence in Figure 4. In Eq. (4) however, $T_s$ implicitly depends on $q$. This dependency is made explicit by writing the stress-strain relation $T = E\pi a^2 \Delta L/L$, where $T$ is the tension in the CNT. $T$ relates to its axial vector component $T_x$ through

$$T_x = T \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]^{1/2},$$
(6)

which one expands as

$$T_x = \frac{E\pi a^2}{L} \int_{-L/2}^{+L/2} dx \sqrt{1 + \left( \frac{dy}{dx} \right)^2} - 1.$$  
(6)

For small deflections of the beam $dy \ll dx$, Eq. (6) writes to second order as

$$T_x = \frac{EI a^2}{2L^2} \chi_p \left( 1 + \frac{1}{18\pi^2} \left( \frac{\Delta P}{E} \right)^2 \rho^6 \right),$$  
(7)

where $\rho = L/a$. Equation (7) was next inserted into Eqs. (4), (5), and (1) to obtain the theoretical piezoresistance. This calculation is the first which considers the present boundary conditions and describes the change of tension with strain. The leading terms in the piezoresistance are
TABLE I. Young’s moduli (E), piezoresistive constants (πL), and CNT radii (a) obtained by fitting Eq. (8) to the piezoresistance data of Fig. 4.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>40 sccm CH₃ E (TPa) πL (TPa⁻¹) a (nm)</th>
<th>60 sccm CH₃ E (TPa) πL (TPa⁻¹) a (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.17 14 11</td>
<td>0.13 13 12.5</td>
</tr>
<tr>
<td>9</td>
<td>0.20 18 11</td>
<td>0.35 28 13</td>
</tr>
<tr>
<td>10</td>
<td>0.24 20 12</td>
<td>0.40 45 13</td>
</tr>
<tr>
<td>11</td>
<td>... ... ...</td>
<td>0.47 50 13</td>
</tr>
<tr>
<td>12</td>
<td>0.47 48 12.5</td>
<td>... ... ...</td>
</tr>
</tbody>
</table>

The quadratic dependence is a consequence of the elongation of the beam. This elongation is independent in which pressure is applied, hence the symmetry with respect to a change in sign of ΔP. At higher pressure, deformation of the CNT means that pressure loading becomes uneven across its length. The saturation of the piezoresistance occurs when loading increases at the centre of the CNT relative to its ends. We used Eq. (8) to fit the data in Fig. 4 and obtain πL, E, and a as adjustment parameters (using L = 1 μm in ρ = L/a). The data are summarized in Table I.

We find that E and πL increase with growth time increasing the device sensitivity as shown in Figure 4 and Table I. Young’s moduli of 0.13-0.47 TPa are lower than the values expected from pristine single wall CNTs, but are in good agreement with the values expected from multi-wall CNTs. The thermo-mechanical annealing of Stone-Wale structural defects and the migration of vacancies and adatoms is likely to explain the increase in Young’s modulus when the growth time increases from 8 min to 12 min. The fit of the piezoresistance data in Figure 4 further yields the radii of CNTs, which are in excellent agreement with radii measured from scanning and transmission electron micrographs (Figure 3(a)). These results validate the assumptions made when building the theory.

In summary, we have grown carbon nanotubes inside a silicon micro-cavity and have evidenced a temperature threshold above which CNTs self-anchor to opposite sides of the cavity and conduct. By applying gas pressure to the cavity, the embedded nanotubes bend causing the resistance to change as predicted by the Euler-Bernoulli theory. Fitting the theory to the experimental data accurately estimates the radius of CNTs, their Young modulus, and piezoresistive constant. The proposed pressure sensor was scaled to a cross-sectional area of 2 μm², which is four orders of magnitude smaller than current membrane sensors.