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Michael A. Cullinan and Martin L. Culpepper

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# Control of carbon nanotube geometry via tunable process parameters

Michael A. Cullinan and Martin L. Culpepper[a)]
*Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

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We present a method for selecting fabrication process parameters (temperature, catalyst film thickness, and hydrocarbon concentration) that may be used to grow multiwalled carbon nanotubes (CNTs) with desired outer diameter $D$ and number of walls $N_w$. This capability enables the control of rigidity, which in turn makes it possible to control a CNT's lateral vibration behavior and bending stiffness. A growth model was generated and used to link $D$ and $N_w$ to the process parameters. Experimental results showed that the models predicted $D$ and $N_w$ with less than 6% and 7% error, respectively. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2979697]

Carbon nanotubes (CNTs) are well suited for use in flexure-based nanomechanical devices because CNTs possess (i) a high elastic modulus (~1 TPa) (Ref. 1) and (ii) failure strains of up to 40%.[2] These properties, combined with CNTs' low mass per unit volume, make it possible for CNT-based devices to exhibit three characteristics that are useful in nanoscale devices: (1) vibration frequencies in lateral bending that may exceed of tens of gigahertz, (2) high energy storage per unit mass, and (3) large ranges of motion relative to their size. These characteristics have led to their use as critical elements of nanoelectromechanical prototypes, for example relays,[3] grippers,[4] resonators,[5] and motors.[6]

A main challenge in realizing a desired performance level is the sensitivity of the lateral bending stiffness to outer diameter,$D$ and wall thickness $t$. The lateral bending stiffness of a cantilevered CNT may be estimated via

$$k = \frac{3\pi E[D^4 - (D-2t)^4]}{64L^3}, \tag{1}$$

where stiffness $k$ depends upon elastic modulus $E$ and tube length $L$. The elastic modulus is a material property and the length of the CNT correlates to the size of the device, therefore manipulating the value of $k$ for a given device size requires manipulation of $D$ and/or the number of walls $N_w$. This letter covers a means to derive empirical equations that may be used to set growth process parameters in order to produce multiwalled CNTs (MWCNTs) with desired $D$ and $N_w$. We demonstrate this with a specific catalyst and carbon source, but the method may be used with other catalysts and carbon sources by creating empirical relationships that correspond to the desired catalyst-source combination.

Our MWCNTs were grown via thermal chemical vapor deposition in a resistively heated furnace that was adapted from a previous design.[7] A 15 nm thick aluminum oxide layer and a layer of iron catalyst were deposited on a silicon substrate via electron beam deposition. The average iron catalyst film thickness $F$ was controlled to within 1 Å using a quartz crystal monitor in the evaporation chamber. The coated substrate was then placed in the furnace and an annealing step was initiated. The temperature of the furnace was increased to 700 °C and held within 10 °C of this value for 15 min. The temperature of the substrate's surface was measured within 1 °C via a $K$–type thermocouple. The substrate temperature was then raised to the growth temperature $T$, and methane was introduced into the system at a volume percentage concentration $C_m$. An argon flow was then adjusted to maintain the total gas flow rate at 1000 SCCM (SCCM denotes standard cubic centimeters per minute at STP). The flow rate was measured within 10 SCCM using a digital mass flow meter. The growth step continued under these conditions for 20 min.

The values of $D$ and $t$ from 30 CNTs were measured with a transmission electron microscope (TEM) at 30 randomly selected locations in the sample. This procedure was repeated for 15 different samples. The values of $D$ and $N_w$ for each sample were found to be normally distributed using the Anderson–Darling test at a 90% test level. Scanning electron microscope (SEM) and TEM images of a typical sample, as well as histograms of $D$ and $t$ of the CNTs from the sample, are shown in Fig. 1. The process parameters for each sample were set using the central composite inscribed experimental design[8] method. The ranges of conditions were (i) 0.5–6 nm for $F$, (ii) 700–900 °C for $T$, and (iii) 37%–100% for $C_m$.

The effects of $C_m$, $F$, and $T$ upon $D$ were first determined. The catalyst film thickness $F$ was the dominant process parameter in determining the value of $D$, accounting for over 90% of the change in $D$. A logarithmic function, of the type that is typically used to relate $D$ and $F$,[9] fit our data with a $R^2$ value that exceeded 0.96.

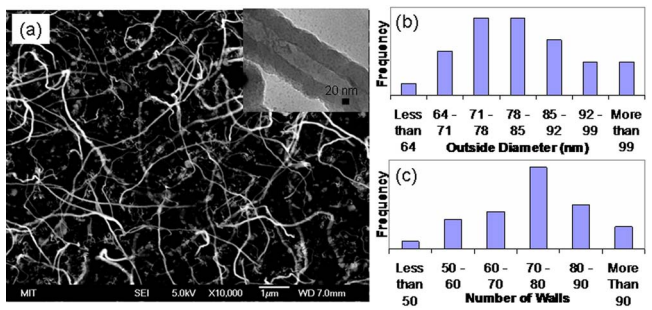


FIG. 1. (Color online) (a) SEM image with inset TEM image of sample from run 15 with $F$=3 nm, $T$=800 °C, $C_m$=68.5%. (b) Histogram of CNT outside diameter for rum 15. (c) Histogram of number of walls in CNT for run 15.

a)Electronic mail: culpepper@mit.edu.

 

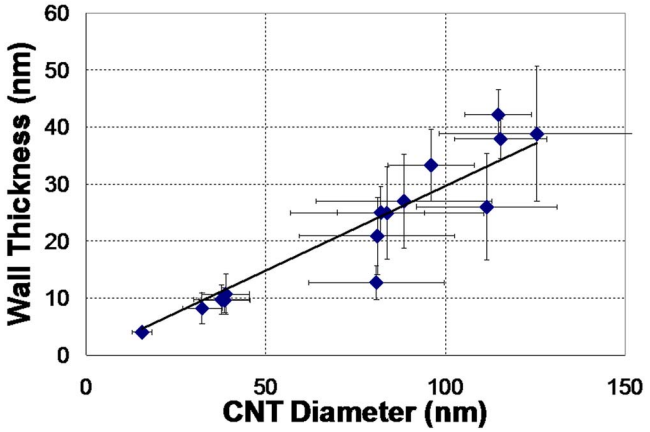


FIG. 2. (Color online) Relationship between the CNTs' $D$ and $t$.

A regression analysis was performed in order to determine the independent effect of the process parameters upon $D$. The variable $C_m$ was not statistically significant and was therefore removed form the regression model. The relationship between $D$, $T$, and the natural log of $F$, was found to be statistically significant at over a 99.99% confidence level. Equation (2) captures the relationship with $D$ and $F$ in nm, and $T$ in °C,

$$D = 43.7\ln(F) + 0.0484T. \tag{2}$$

The effects of $C_m$, $F$, and $T$ upon $t$ were next determined. The value of $t$ ranged from 4 to 40 nm depending upon process parameter settings. As shown in Fig. 2, the value of $t$ generally increases as $D$ increases. This is expected as more shell walls are required to create larger-diameter CNTs. The error bars in Fig. 2 represent the 95% confidence intervals for the 30 measurements that were taken within each sample. The largest source of error in $D$ and $t$ was found to be the dewetting of the catalyst film into nanoparticles. This process is difficult to control because small variations in the initial film structure may result in large differences in the final nanoparticle size, and therefore CNT diameter. The average standard deviation in the catalyst nanoparticles across all films was found to be 13.4% of the average catalyst particle size. The error bars in Fig. 2, therefore, increase in size as the value of $F$ increases. The TEM used to make these measurements resolves linear dimensions within 0.4 nm, which is equivalent to a measurement error of 2%–7% depending on the CNT diameter and wall thickness. Therefore, the error associated with the measurement system is small when compared to the dewetting-induced variance within a sample.

The values of $T$ and $C_m$ should affect $t$ because the diffusion rate of the carbon into the catalyst affects the wall thickness[10] and is the rate depends upon $T$ and $C_m$. The values of $T$ and $C_m$ were, therefore, included in the regression model. The regression showed that all of the process parameters have a statistically significant effect at a 99.99% confidence level. A design equation was generated to capture the relationship between process parameters and $t$. In Eq. (3) $t$ and $D$ are in nanometers, $T$ is in °C, and $C_m$ is in percent. The variable $D$ is used in Eq. (3) in place of $F$ to link the two design variables $D$ and $t$. Note that both variables could not be used due to their high degree of colinearity,

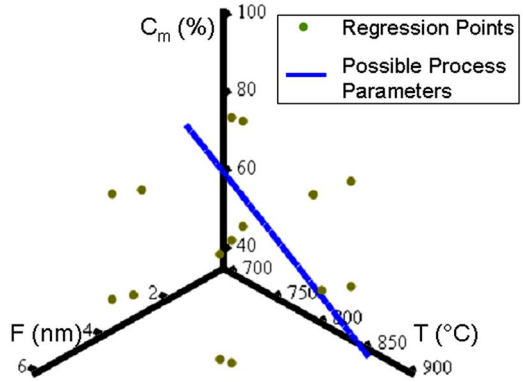


FIG. 3. (Color online) Set of suitable process parameters for $D=58$ nm and a $t=15$ nm.

$$t = -38.3 + 0.307D + 0.0316T + 0.166C_m. \tag{3}$$

Equation (3) may be modified to set $N_w$ if the value of $t$ is divided by the thickness of one shell wall,

$$N_W = -112.6 + 0.903D + 0.0929T + 0.488C_m. \tag{4}$$

Equations (2) and (3) were used to design a growth process wherein the goal was to produce CNTs with $D=58$ nm and $t=15$ nm ($N_w=44$). The set of suitable process parameters for $D=58$ nm and a $t=15$ nm are shown in Fig. 3 along with the regression points from the central composite inscribed experimental design. Process parameters $F=1.6$ nm, $T=774$ °C, and $C_m=66.2\%$ were selected and tested from the set of suitable process parameters because they represented a midrange value for $T$ and $C_m$. The results of this process are listed in Table I. The measured results are the average values and the 95% confidence intervals of the 30 measurements taken within each sample. The predicted results are within the 95% confidence interval of the measured values for $D$, $t$, and $N_w$. The variance within a sample is primarily caused by the dewetting of the catalyst film during the annealing process. The average error between the measured and predicted results is less than 7%.

The preceding shows that the equations/methods may be used to design CNTs with desired lateral stiffness. For example, one may want a linear flexural bearing for which $k=2.1$ N/m. Consider a device that is composed of a $5\times5\times500$ $\mu$m$^3$ silicon stage that is connected to ground by four 5 $\mu$m long CNTs. For $E=1$ TPa,[1] the desired values of $D$ and $t$ may be calculated via[11]

$$k = \frac{3\pi E[D^4 - (D-2t)^4]}{4L^3}. \tag{5}$$

There are several sets of fabrication process parameters that would produce CNTs that yield a desired stiffness. The data from our study indicate that it is possible to minimize the variance in $t$ by using the set of process parameters that yield the MWCNT with the lowest Gibbs free energy.[12] This

TABLE I. Results of test growth.

| | Desired | Measured | Error |
|---|---|---|---|
| $D$ | 58 nm | $61.2\pm7.4$ nm | 5.52% |
| $t$ | 15 nm | $16.0\pm3.3$ nm | 6.25% |
| $N_W$ | 44 | $47\pm10$ | 6.82% |

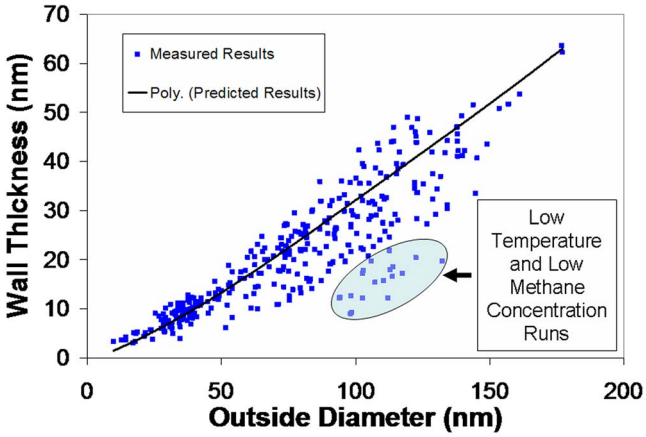


FIG. 4. (Color online) Thermodynamic model predictions vs measured values.

is expected as the wall thickness that minimizes energy is the most stable wall thickness. This means that influences that would lead to variation in wall thickness are most highly resisted. The Gibbs free energy is the sum of the surface energy, the strain energy, and the change in the chemical potential energy that is required to create the CNT:[13]

$$\Delta G = 2\pi\sigma(D-t)dl + \frac{1}{12}\pi E a^2 \ln\left(\frac{D}{D-2t}\right)dl - \frac{\pi\Delta\mu_o}{4\Omega}[D^2-(D-2t)^2]dl. \quad (6)$$

In Eq. (6), $\Delta G$ is the Gibbs free energy, $\sigma$ is the energy required to form graphite, $dl$ is the differential length of the CNT, $\Delta\mu_o$ is the chemical potential change for the formation of the CNT, $\Omega$ is the volume of carbon atoms, and $a$ is the graphite interplanar spacing. Values for $\sigma$, $\Delta\mu_o$, $\Omega$, $a$, and $E$ were taken from Refs. 13 and 14. For a given value of $D$, the derivative of the Gibbs free energy with respect to $t$ may be set to zero and then the equation may be solved for the value of $t$ that minimizes the Gibbs free energy.

The preceding procedure was used to calculate values of $t$ for several growth processes parameter sets that were characterized in this study. A comparison of the predicted and measured results may be seen in Fig. 4. The CNTs that were grown at low values of $T$, and/or at low values of $C_m$, are highlighted in the figure. They fall well below the values that were predicted by the thermodynamics of the reaction, and this indicates that the reaction kinetics have a large effect upon the value $t$.[12]

TABLE II. Results of growth for linear flexural bearing.

| | Desired | Measured | Error |
|---|---|---|---|
| $D$ | 104.7 nm | $104.3 \pm 5.4$ nm | 0.38% |
| $t$ | 25.0 nm | $25.6 \pm 1.3$ nm | 2.40% |
| $k$ | 2.10 N/m | $2.11 \pm 0.40$ N/m | 0.48% |

TABLE III. Frequency test growths.

| | Desired $\omega$ | Calculated $\omega$ | Error |
|---|---|---|---|
| Flexural Bearing | 27 kHz | $27.4 \pm 5.7$ kHz | 1.48% |
| Resonator | 183 GHz | $186 \pm 15$ GHz | 1.64% |

The energy minimization procedure was used to formulate a set of process parameters that would grow CNTs for the linear flexural bearing. The process parameters were (i) $F=5$ nm, (ii) $T=710$ °C, and (iii) $C_m=52.4\%$. From Eqs. (2) and (3), we would expect that these conditions would yield $D=104.7$ nm and an inside diameter of 25.0 nm. The results of this growth process may be seen in Table II. The values of $k$ that were calculated using the measured geometry differ from the desired values of $k$ by less than 0.5%.

A similar method was used to grow CNTs with desired natural frequency in a lateral bending mode $\omega$. For example, a 100 nm long resonator with a natural frequency of 183 GHz could be produced by using a CNT with $D=90.6$ nm and $t=27.6$ nm. This may be achieved by using $F=3$ nm, $T=880$ °C, and $C_m=61.5\%$. The results for this growth process, and for the flexural bearing, may be seen in Table III. Each of the frequencies calculated from the measured CNT geometries is within the 95% confidence interval of the desired frequency. The maximum error between the desired frequency and the calculated frequency was less than 2%.

In this paper, we have shown that it is possible to control the geometry of CNTs by tuning fabrication process parameters. This should enable the design and fabrication of CNTs that possess well-defined flexural characteristics. This process may be used to create CNTs for nanoelectromechanical system devices that possess desired vibration, deflection, and lateral stiffness characteristics.

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