Multiwall carbon nanotube resonator for ultra-sensitive mass detection

W. Wu, M. Palaniapan and W.-K. Wong

The experimental realisation of a multiwall carbon nanotube (MWNT) resonator for mass sensing applications is reported. Fabricated MWNT resonators with length, inner radius and outer radius as 34.37 µm, 5.37 nm and 13.27 nm, respectively, had a measured resonant frequency around 110–120 kHz. Measured results indicate that these MWNT resonators exhibit sub-attogram responsivity.

Introduction: Resonance-based microelectromechanical sensors offer the potential of meeting the high-performance requirement of various applications, including biomedical sensors and mass detectors, etc. [1]. Frequency shift in resonators due to mass loading is utilised in these applications. The reported detectable mass can be as small as several femtograms by using microsized silicon cantilevers [2]. However, the demands on emerging applications such as gas detection require even higher sensitivity. Since their discovery in 1991 [3], the extraordinary mechanical and electrical properties have made carbon nanotubes (CNTs) ideal candidates for ultra-sensitive nano-devices. In this Letter, we report the experimental realisation of a CNT mass sensor and investigate the capability of a multiwall carbon nanotubes (MWNTs) mass sensor which exhibits sub-attogram mass responsivity.

Fig. 1 Experimental setup of individual MWNT resonator, and SEM and TEM micrographs of individual MWNT resonator and its structural parameters

a) Experimental setup
b) SEM and TEM (inset) micrographs

Resonator fabrication and experimental setup: The catalytic chemical vapour deposition method is adopted to grow the MWNTs used in this work. The MWNTs are grown on <111>-oriented boron-doped silicon substrate using Fe as catalyst. Decomposition of acetylene gas provides the carbon source for the assembly of the MWNTs. Fig. 1a shows the experimental setup for an individual MWNT resonator, which is actuated electrostatically by applying a DC bias (V_p = 5 V) and a sine wave signal (V_p-p = 50 mV) between the tungsten counter electrode and the Si substrate. By adjusting the frequency of the sine wave signal, the MWNT resonator can be actuated and maximum amplitude is achieved when the drive signal frequency matches the mechanical resonance frequency of the MWNT resonator.

The in situ observation of nanotube resonance is conducted with a scanning electron microscope (FEI XL30 FEG SEM) at working pressure around 10⁻⁶ mbar. The resonance can be acquired when the laterally resonating nanotube traverses the electron beam. The structural parameters of the MWNT resonator are obtained through transmission electron microscope (TEM) analysis. The length (L), inner radius (r_i) and outer radius (r_o) of this MWNT resonator are measured as 34.37 µm, 5.37 nm and 13.27 nm, respectively, as shown in Fig. 1b.

Experimental results and discussion: Theoretically, the resonant frequency depends on the nanotube outer diameter (D_o = 2r_o), length (L), density (ρ), and bending modulus (E) of the nanotube as shown in [4]:

\[ f_1 = \frac{\beta_1}{8\pi^2} \sqrt{\frac{(D_o^2 + D_i^2)E}{\rho}} \]  

(1)

\[ k = \frac{3E}{L^2} (r_o^4 - r_i^4) \]  

(2)

where k is spring constant, ρ_{MWNT} = 1.35 g/cm³, β_1 = 1.875.

Fig. 2 Amplitude of MWNT resonator against frequency
Inset: SEM micrograph of MWNT resonator at resonance peak 1

Fig. 2 shows the plot of amplitude against drive frequency in both the forward and the backward process (i.e. frequency is increased and decreased). Resonance peak 1 is observed at 109.606 kHz in forward process while resonance peaks 2, 3, 4 are observed at 108.680, 79.880 and 74.073 kHz successively in the backward process. The starting time of the experiment, when drive frequency is 0 kHz in the forward process, is recorded as t = 0 min and the corresponding time when the above four resonance peaks are observed is 10, 11, 44, 57 min, respectively. The resonance frequency shift can be investigated by transforming (1) into

\[ f_1 = \frac{1}{2\pi} \sqrt{\frac{k + \Delta k}{m + \Delta m}} \]  

(3)

In (3), k and m are the spring constant and mass of the original pristine MWNT resonator before the actuation and measurement started. Δk and Δm are the variations in k and m during the actuation and measurement. It was found in the experiment that the electron-beam-induced deposition (EBID) of carbonaceous substances onto the MWNT inside the vacuum chamber of the SEM is the main cause resulting in the variations of k and m which was observed in [5]. It was also found that, when deposited carbonaceous substances are localised near the free end of the MWNT resonator, the variation in k becomes more significant compared to m which was observed in [5]. Micrographs of the MWNT resonator after the experiment indicate that the EBID of carbonaceous substances is mostly confined near the free end of the MWNT as can be seen in insets of Fig. 3. It is therefore reasonable to assume that δk of the MWNT resonator system can be neglected in the subsequent analysis and, hence, (3) is transformed into (4) as

\[ f_1 = \frac{1}{2\pi} \sqrt{\frac{k}{m + \Delta m}} \]  

(4)

It can be concluded from (2) that the bending modulus (E) of the MWNT resonator remains constant and can be determined as 1.41 TPa by substituting the frequency value of the resonance peak 1 into (1). Spring constant k is subsequently calculated using (2) as

ELECTRONICS LETTERS 28th August 2008 Vol. 44 No. 18
9.878 × 10^{-6} \text{ N/m}. The calculated bending modulus and spring constant values are of the same order as previously reported in experimental and calculation results of 1.8 TPa \[6\] and 4.6 × 10^{-6} \text{ N/m} \[7\], respectively.

Conclusions: We have examined the potential of the MWNT as an ultra-sensitive mass sensor and MWNT nanoelectromechanical resonator which can detect mass variations in the sub-attogram (10^{-18} \text{ gram}) range reported in this Letter. The performance of the MWNT mass sensor can be enhanced further with the advancement of fabrication and fully-electrical integration of the MWNT sensor system. Nevertheless, results from our experiments indicate that the MWNT nanoelectromechanical mass sensor can provide significant advances in chemical and biological sensing and offer near-term prospects for mass sensing of individual molecules in these applications.

The effective mass of the MWNT resonator system at each resonance peak is calculated and tabulated in Table 1. This linear \( m - t \) relationship (Table 1) makes it reasonable to assume that of the same relationship also holds true before the first resonance peak is observed. Therefore, the mass of the pristine MWNT (P-CNT) can be obtained by extrapolating the linear \( m - t \) relationship when \( t = 0 \), which turns out to be 15.51 attogram. The fundamental resonant frequency for the pristine MWNT hence can be calculated as 127.013 kHz. The responsivity of the MWNT resonator system (\( \Delta f/\Delta m \)) is obtained by linearly fitting the curve of effective mass against resonant frequency. The value of \( \Delta f/\Delta m \), which is the absolute value of the slope of the linear curve, is obtained as 1668.49 Hz/attogram. This shows that the MWNT resonator under investigation has high responsivity owing to the extremely small system mass. However, these values are not the actual sensitivity of the MWNT resonator, which depends on the signal processing capability available which will be the focus of our future work.

The effective mass for MWNT resonator system

\[
\text{Effective mass of MWNT resonator system} = \frac{k}{4\pi^2f^2}
\]

Table 1: Effective mass for MWNT resonator

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>109.606</td>
<td>108.680</td>
<td>79.880</td>
<td>74.073</td>
</tr>
<tr>
<td>10</td>
<td>127.013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>15.51</td>
<td>20.82</td>
<td>45.60</td>
</tr>
<tr>
<td>44</td>
<td></td>
<td>21.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td></td>
<td>39.21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The curve of effective mass against resonant frequency. The value of \( \Delta f/\Delta m \), which is the absolute value of the slope of the linear curve, is obtained as 1668.49 Hz/attogram. This shows that the MWNT resonator under investigation has high responsivity owing to the extremely small system mass. However, these values are not the actual sensitivity of the MWNT resonator, which depends on the signal processing capability available which will be the focus of our future work.

Conclusions: We have examined the potential of the MWNT as an ultra-sensitive mass sensor and MWNT nanoelectromechanical resonator which can detect mass variations in the sub-attogram (10^{-18} gram) range reported in this Letter. The performance of the MWNT mass sensor can be enhanced further with the advancement of fabrication and fully-electrical integration of the MWNT sensor system. Nevertheless, results from our experiments indicate that the MWNT nanoelectromechanical mass sensor can provide significant advances in chemical and biological sensing and offer near-term prospects for mass sensing of individual molecules in these applications.

© The Institution of Engineering and Technology 2008
4 July 2008
Electronics Letters online no: 20081932
doi: 10.1049/el:20081932
W. Wu, M. Palaniapan and W.-K. Wong (Department of Electrical and Computer Engineering, National University of Singapore, Singapore)
E-mail: elemp@nus.edu.sg

References
4 Rao, S.S.: ‘Mechanical vibrations’ (Addison-Wesley, 1995), Chap. 8, pp. 523–527