Nanowire as pico-gram balance at workplace atmosphere

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Abstract

The mechanical resonance behavior of a ZnO nanowire/nanorod at ambient condition has been studied under optical microscope by cutting its length using focused ion beam microscopy. Nanobalance using a ZnO nanowire as the cantilever has been demonstrated for measuring the mass in the order of pico-grams in working atmosphere (see optical microscopy images). The measurement limit of the balance is estimated to be \(\sim 1 \text{ pg}\). The technique demonstrated here has potential for commercial applications in general laboratories, especially for measuring the mass of wet biological cells or species.

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1. Introduction

One-dimensional (1D) nanostructures have been the dominant materials for investigating various nano-scale phenomena, from carbon nanotubes [1–3] to semiconducting nanowires [4,5] and to ZnO nanobelts [6]. A natural application of 1D nanomaterials is as cantilevers due to the large aspect ratio [7,8]. Mechanical resonance of a carbon nanotube was first demonstrated using in situ transmission electron microscopy (TEM), [8] in which the resonance was observed directly under the electron beam imaging. A nanobalance based on a single nanotube was demonstrated for measuring the mass of a tiny particle in the order of \(\sim 22 \text{ fg}\) [8,9]. ZnO nanobelts have also been shown to behave as dual-mode nano-oscillators [10]. All of these observations were carried out using in situ TEM or in situ SEM [11], in which the 1D nanostructure was magnified large enough for direct observation, and more importantly, the experiments were conducted in a vacuum of \(\sim 10^{-4}-10^{-6} \text{ Torr}\) and the resonance was observed with the assistance of electron microscopy.

Using lithography fabricated cantilevers in an AFM apparatus, ultrasensitive nanobalance has been demonstrated for measuring a tiny mass at a sensitivity of 0.2 ag [12] and 100 ag [13] under vacuum conditions of \(10^{-7}\) and \(10^{-8} \text{ Torr}\), respectively. For practical applications, nano-oscillators may be required to operate in workplace atmosphere. It is known that, under ambient conditions, the high viscosity of the environment greatly damped the resonance, thus, the performance of the resonator is greatly reduced [14]. Using the AFM based approach and at ambient condition, cantilever based nanobalance has been remarkably demonstrated for measuring a mass in the order of 160 ag [15] and 6 pg [16].

In this paper, we report an alternative approach of using nanowires as nano-oscillator for measuring tiny mass at ambient condition, which is simple and much lower cost than the AFM based technique. The resonance was induced by an external electric field, and the resonance was observed using a conventional optical microscope. A tiny particle was placed at the tip of the cantilever, and a balance has been
demonstrated for measuring a tiny mass in pico-gram range. The measurement limit of the balance at workplace atmosphere is estimated to be $\sim 1$ pg.

2. Experimental

ZnO nanowires/nanorods were synthesized by a vapor–solid growth process. Individual ZnO nanowires were manipulated by a pin and placed on a silicon substrate with one end being fixed by silver paste. Then the ZnO nanowire cantilever was placed to the middle position between the two electrodes. The electrodes and resonator are located in the focal plate of the optical microscope. The measurement is based on the mechanical resonance of the ZnO nanowire cantilever induce by electric field under ambient condition. A constant voltage $V_{dc}$ and an oscillating voltage $V_{ac} \sin \omega t$ with tunable frequency were applied between the electrodes to stimulate the cantilever. The dimensions of the cantilever were measured by field emission scanning electron microscopy (FE-SEM). The dynamic behavior of the cantilever was observed under an optical microscopy with a maximum magnification of $\times 1000$, and recorded using a CCD camera that was attached to the optical microscopy. The amplitude–frequency response of the cantilever was obtained by measuring the resonance amplitude of the cantilever by varying the driving frequency $\omega$. The length of the nanowire was cut by a focus ion beam (FIB) microscopy (NOVA, FEI), and in order to present the application of the cantilever as a balance, a tiny Pt short segment was built at the very end by depositing Pt using an FIB.

3. Results and discussion

Fig. 1(a) shows the experimental set up used in our experiment. The imaging system and the driving electric source are displayed in Fig. 1(b). Fig. 1(c) is the enlarged image of the square-enclosed area in Fig. 1(a), displaying the simplicity of the experiments. Fig. 1(d) is the circuit diagram of the set up. Fig. 1(e) shows a low magnification SEM image of a ZnO nanowire cantilever with length $L$ of 143 $\mu$m. Higher magnification SEM image (Fig. 1(f)) shows that the ZnO nanowire cantilever has a uniform shape along its entire length. Fig. 1(g) shows the tilted SEM image of the cantilever, displaying the hexagonal cross-section of the ZnO nanowire with side width $a$ of $\sim 192$ nm. Fig. 1(h) shows a geometrical model for the calculation of the moment of inertia $I$ of the cantilever based on the experimental set up and our SEM observation.

Fig. 2(a) shows an optical microscope image of a stationary ZnO nanowire cantilever. By changing the frequency of the oscillating voltage, the first harmonic resonance with vibration plane perpendicular to the viewing direction can be observed (Fig. 2(b)), from which the amplitude of the resonance was measured. Fig. 2(c) shows a frequency response curve of a ZnO nanowire cantilever ($L = 109.2$ $\mu$m, $a = 305$ nm) in air, obtained with $V_{dc} = 28$ V and $V_{ac} = 10$ V. The $Q$ factor is about 5, which agrees to the experimental and theoretic calculated results of others [14,17].

As expected, the short cantilevers have a higher resonance frequency than the longer cantilevers. A ZnO nanowire cantilever with length of 145.7 $\mu$m and side width of 309 nm was used to study the dependence of resonance frequency on its length. The length of the nanowire was cut by a focus ion beam (FIB) microscopy into a sequence of lengths of 117.8 $\mu$m, 103.7 $\mu$m, and 88 $\mu$m, respectively. At each length, the resonance profile was obtained at ambient condition. As shown in Fig. 3(a), when the length of the cantilever was 145.7 $\mu$m, the resonance frequency was $\sim 14$ kHz; and when the length was 88 $\mu$m, the resonance frequency was increase to $\sim 40.2$ kHz. The resonance frequency $f$ is scaled linearly with $L^{-2}$ (Fig. 3(b)). This is exactly the expected resonance result from the classical equation of one-end affixed cantilever [18]:

$$f = \frac{\rho_i^2}{2\pi L^2} \sqrt{\frac{E}{m}}$$  \hspace{1cm} (1)
Fig. 2. Optical microscopy images of a ZnO nanowire cantilever at (a) stationary, (b) the first harmonic resonance; (c) the frequency response curve of the ZnO nanowire cantilever in air with excitation voltages of $V_{dc} = 28$ V and $V_{ac} = 10$ V.

Fig. 3. (a) Series frequency response curves of the same ZnO cantilever after sequentially cutting its length by a focused ion beam microscopy. (b) Resonance frequency $f$ vs $L^{-2}$ plot, showing a linear relationship as expected theoretically.

where $\beta_i$ is a constant for the $i$th harmonic: $\beta_1 = 1.875$, and $\beta_2 = 4.694$, $E$ is the elastic modulus, $m$ is the unit length mass, and $L$ is the length of the cantilever.

In our case, the cantilever has a hexagonal cross-section, by using the model of moment of inertia $I_{xy}$ shown in Fig. 1(h), we can calculate the $I_{xy}$ and $m$:

$$I_{xy} = \frac{5\sqrt{3}}{16} a^4$$  \hspace{1cm} (2)

$$m = \frac{3\sqrt{3}}{2} a^2 \rho$$  \hspace{1cm} (3)

where $a$ is the side width of the hexagonal cantilever, and $\rho$ is the density of ZnO. Inserting Eqs. (2) and (3) into Eq. (1), we can obtain:

$$f = \frac{\beta^2 a}{4\pi L^2} \sqrt{\frac{5E_{xy}}{6\rho}}$$  \hspace{1cm} (4)

$$E_{xy} = \frac{96\pi^2 \rho L^4 f^2}{5\beta^4 a^2}.$$  \hspace{1cm} (5)

Based on the experimentally measured data, the elastic modulus of the ZnO nanowire cantilevers were calculated using Eq. (5), as summarized in Table 1, where the cantilevers’ dimensions, resonance frequency, and elastic modulus are listed for 15 ZnO nanowire cantilevers. The average elastic modulus is $\sim 106$ GPa, which is about 2–3 times larger than that of either the ZnO nanobelts [10] or the small size nanowires [19], but

<table>
<thead>
<tr>
<th>$N$</th>
<th>Length $L$ (µm)</th>
<th>Side length $a$ (nm)</th>
<th>Resonance frequency (kHz)</th>
<th>Elastic modulus $E_{xy}$ (GPa)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>102.8</td>
<td>457.4</td>
<td>51</td>
<td>119.3</td>
</tr>
<tr>
<td>2</td>
<td>254.2</td>
<td>470</td>
<td>9.25</td>
<td>121.1</td>
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<tr>
<td>3</td>
<td>109.2</td>
<td>305</td>
<td>31</td>
<td>127.1</td>
</tr>
<tr>
<td>4</td>
<td>102.7</td>
<td>307</td>
<td>34</td>
<td>117.4</td>
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<tr>
<td>5</td>
<td>215.8</td>
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<td>8</td>
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<td>6</td>
<td>110.4</td>
<td>515.8</td>
<td>47.5</td>
<td>107.7</td>
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<tr>
<td>7</td>
<td>150</td>
<td>288</td>
<td>11.5</td>
<td>69.4</td>
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<td>8</td>
<td>143</td>
<td>192</td>
<td>10</td>
<td>97.5</td>
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<td>9</td>
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<td>262.2</td>
<td>9</td>
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<td>42.5</td>
<td>138.2</td>
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<tr>
<td>15</td>
<td>170.7</td>
<td>376.8</td>
<td>11</td>
<td>62.5</td>
</tr>
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</table>
in the range of early reported results for thin films [20]. The nanowire used here grows along [0001], while the nanobelt measured previously along [01\(\bar{1}10\)] or [21\(\bar{1}0\)]; and the nanowire is a lot larger than the dimension of the nanobelt. Therefore, it is suggested that the difference in the elastic modulus between the ZnO nanowire and nanobelt may be caused by the anisotropic structure of ZnO, their sizes and possibly geometrical shapes.

After calibrating the theory for nanocantilever, we now present the application of the cantilever as a balance. Before placing a tiny mass at its tip, the resonance vibration behavior of a ZnO nanowire cantilever with length \(L\) of 103.0 \(\mu\)m and side width of 385 nm was carefully studied. Fig. 4(b) and (c) shows the stationary and resonance vibration optical microscope images, respectively, of the cantilever at ambient condition. The corresponding frequency response plot was shown in Fig. 4(a), with the resonance frequency at \(\sim 46.3\) kHz. Then, a tiny Pt short segment was built at the very end by depositing Pt using an FIB. As shown in Fig. 4(d), the Pt particle has a rod-shape of length 2.05 \(\mu\)m, width 373 nm and thickness 1.75 \(\mu\)m. Fig. 4(e) and (f) show the stationary and resonance vibration optical microscope images of the cantilever with the Pt particle at the tip, respectively. The frequency response curve shown in Fig. 4(a) indicates that the resonance frequency decreased to \(\sim 38.25\) kHz. The shift in resonance frequency can be used to calculate the mass of the Pt particle.

For the harmonic resonance, the mass of the Pt particle is given by: [21,22]

\[
M_{\text{eff}} = M_p \left( \frac{x}{l} \right)
\]

where \(M_{\text{eff}} = M_p \left( x/l \right)\) is the effective mass of the loading material to the cantilever, \(M_p\) is the mass of the loading particle that is located at a distance \(x\) from the base of the cantilever, \(l\) is the length of the cantilever, the \(M_0\) is the mass of the bare cantilever, and \(f_0\) is the resonance frequency of the native cantilever, and \(f\) is the resonance of the cantilever with the particle.

The mass of the Pt particle was found to be \(M_p \sim (2.6 \pm 1) \times 10^{-11}\) g = (26 \pm 1) pg. This value is very close to that calculation from the shape of the Pt particle, which is \(M_p \sim 28.7\) pg by using bulk density, showing the accuracy and reliability of the measurement.

The sensitivity of the mass measurement can be estimated as follows. From Eq. (6) for \(x = l\):

\[
\Delta M_p \approx -\frac{6}{\beta^4} \frac{\Delta f}{f}.
\]

From Fig. 2(b), the accuracy for measuring the frequency shift is \(\sim 0.5\) kHz. At \(f = 40\) kHz and for the first harmonic mode, \(\Delta M_p \approx 0.006M_0\). For a typical nanowire with \(M_0 = 2 \times 10^{-10}\) g, the smallest mass that can be measured is \(1.20 \times 10^{-12}\) g (1.2 pg).

To improve the sensitivity of the nanobalance, one possibility is to use smaller size nanowires. This is possible if the manipulation of a single nanowire can be handled under optical microscope. The detection of resonance can be automated with the use of digital optical imaging and image processing software. It is thus possible to be applied commercially.
4. Summary

In conclusion, the resonance behavior of a hexagonal ZnO nanowire cantilever was studied under ambient condition using optical microscopy. The resonance can be quantitatively described using the classical elasticity theory for the nanowires we have considered. For the [0001] ZnO nanowires of length ~100 µm and diameter ~500 nm, the elastic modulus of the ZnO nanowire was ~106 GPa. The cantilever can also be used as pico-gram balance, which can have a mass measurement sensitivity of ~1 pg. The technique offers the possibility of measuring the mass of wet biological species.

Acknowledgments

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References

[22] The resonance frequency for the combined system of the cantilever and the particle is calculated by splitting the cantilever and the particle into two components. As described in Ref. [16], the resonance frequency for an one-end affixed uniformly cantilever beam is given by:

\[ f_0^2 = \frac{\beta^4}{4\pi^2} \left( \frac{E I}{M_0 l^3} \right) \]

where \( M_0 \) is the mass of the cantilever beam, and \( l \) is the length of the cantilever.

For a particle of mass \( M_p \), attached at a distance \( x \) from the base of the cantilever, if one ignores the mass of the cantilever and only consider its elasticity, the resonance frequency for the system composed of the particle and the weightless cantilever beam is

\[ f_1^2 = \frac{3EI}{M_{eff} l^3} \]

where \( M_{eff} = M_p(x/l) \) is the effective mass of the loading material to the cantilever.

According to the Dunkerley’s formula, the resonance frequency of the system composed of a uniform cantilever beam having mass of \( M_0 \) and a particle with concentrated mass \( M_p \) is

\[ f^2 = \frac{f_0^2 f_1^2}{f_0^2 + f_1^2} = \frac{3f_0^2}{f_0^2 + \frac{f_0^2 M_{eff}}{M_0} + 3} \]

Thus the effective mass \( M_{eff} \) of the particle is given by

\[ M_{eff} = \frac{3M_0}{\beta^4} \left[ \left( \frac{f_0}{f} \right)^2 - 1 \right] \]