Available online at www.sciencedirect.com
SCIENCE DIRECT®
Solid State Communications 139 (2006) 222–226
solid state communications
www.elsevier.com/locate/ssc

# Nanowire as pico-gram balance at workplace atmosphere

Jun Zhou[a,b], Chang Shi Lao[a], Puxian Gao[a], Wenjie Mai[a], William L. Hughes[a], Shao Zhi Deng[b], Ning Sheng Xu[b,**], Zhong Lin Wang[a,*]

[a] *School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA*
[b] *School of Physics and Engineering, State Key Lab of Optoelectronic Materials and Technologies, Guangzhou Province Key Laboratory of Display Materials and Technologies, SunYat-Sen (Zhongshan) University, Guangzhou, 510275, China*

Received 29 May 2006; accepted 3 June 2006 by A.H. MacDonald
Available online 21 June 2006

**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 ∼1 pg. The technique demonstrated here has potential for commercial applications in general laboratories, especially for measuring the mass of wet biological cells or species.


*PACS:* 62.40.+i; 85.85.+j

*Keywords:* A. ZnO nanowires; D. Picogram balance; D. Workplace atmosphere

## 1. Introduction

One-dimensional (1D) nanostructures have been the dominant materials for investigating various nano-scale phenomena, from carbon nanotubes [1–3] to seconducting 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 ∼22 fg [8,9]. ZnO nanobelts have also been shown to behave as dual-mode nanoresonators [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 $\sim 10^{-4}$–$10^{-6}$ Torr and the resonance was observed with the assistance of electron microscopy.

Using lithiography 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 $10^{-8}$ Torr, respectively. For practical applications, nanoresonators 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 nanoresonator 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

** Corresponding author.
* Corresponding author. Tel.: +1 4048948008; fax: +1 4048948008.
*E-mail addresses:* stsxns@zsu.edu.cn (N.S. Xu), zhong.wang@mse.gatech.edu (Z.L. Wang).

0038-1098/$ - see front matter 
doi:10.1016/j.ssc.2006.06.004

demonstrated for measuring a tiny mass in pico-gram range. The measurement limit of the balance at workplace atmosphere is estimated to be ∼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 ×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 μm. 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 ∼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 μm, $a$ = 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

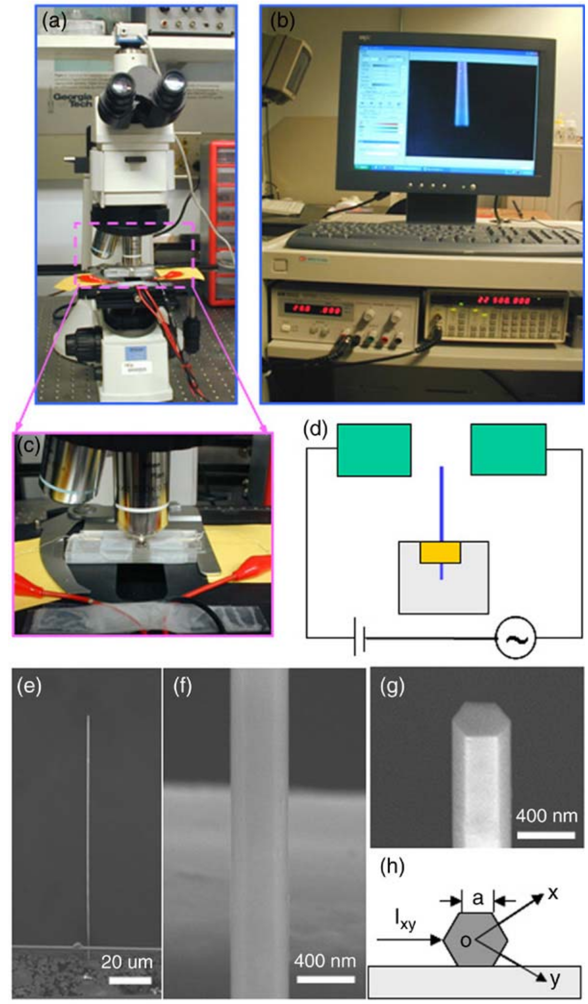


Fig. 1. (a) The optical microscope with the resonator at the focal plate for the resonance measurement of ZnO nanowire. (b) The electronic control and imaging system, where a vibrating nanowire is shown. (c) Enlarged image of the square-enclosed area in (a), for illustrating the simplicity of the experiments. (d) Circuit diagram of the experimental setup for the ZnO nanowire based pico-gram balance. (b) Low magnification and (c) high magnification SEM images of the ZnO nanowire cantilever; (d) Tilted cross-sectional SEM image of the cantilever; (e) Geometrical model for the calculation of the moment of inertia $I$ of the cantilever.

cantilever with length of 145.7 μm 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 μm, 103.7 μm, and 88 μm, 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 μm, the resonance frequency was ∼14 kHz; and when the length was 88 μm, the resonance frequency was increase to ∼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]:

$$f = \frac{\beta_i^2}{2\pi L^2}\sqrt{\frac{EI}{m}} \quad (1)$$

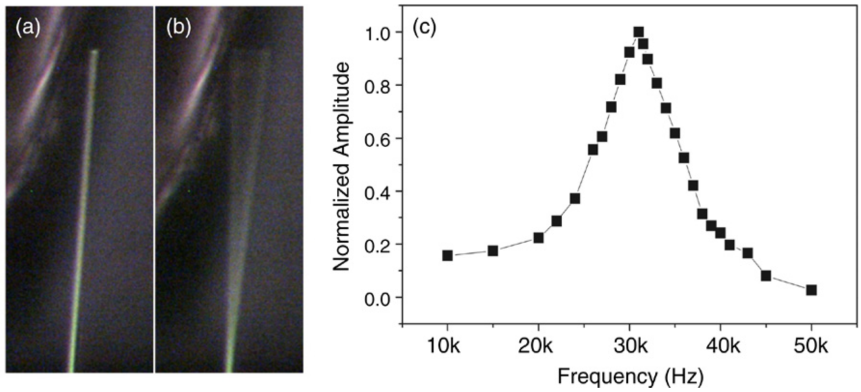


Fig. 2. Optical microscopy images of a ZnO nanowire cantilever at (a) stationary, (b) the first harmonic resonance; (c) the frequency response curve of the ZnO nanowire cantilever in air with excitation voltages of $V_{dc} = 28$ V and $V_{ac} = 10$ V.

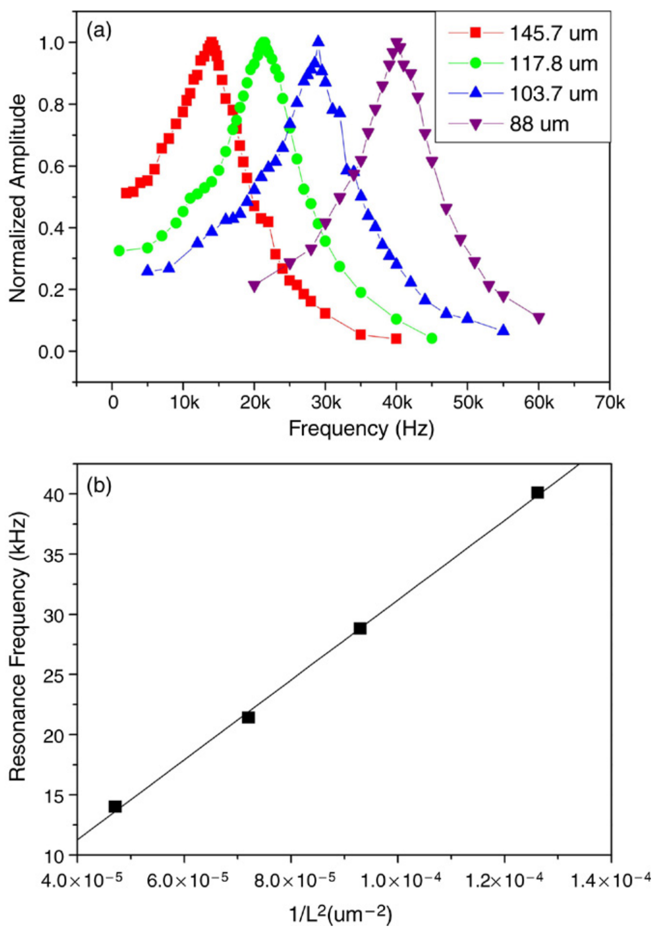


Fig. 3. (a) Series frequency response curves of the same ZnO cantilever after sequentially cutting its length by a focused ion beam microscopy. (b) Resonance frequency $f$ vs $L^{-2}$ plot, showing a linear relationship as expected theoretically.

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 $m$:

Table 1
Dimensions, resonance frequency, and elastic modulus of the large-size ZnO nanowire cantilevers

| $N$ | Length $L$ (μm) | Side length $a$ (nm) | Resonance frequency (kHz) | Elastic modulus $E_{xy}$ (GPa) |
|---|---|---|---|---|
| 1 | 102.8 | 457.4 | 51 | 119.3 |
| 2 | 254.2 | 470 | 9.25 | 121.1 |
| 3 | 109.2 | 305 | 31 | 127.1 |
| 4 | 102.7 | 307 | 34 | 117.4 |
| 5 | 215.8 | 307 | 8 | 104.4 |
| 6 | 110.4 | 515.8 | 47.5 | 107.7 |
| 7 | 150 | 288 | 11.5 | 69.4 |
| 8 | 143 | 192 | 10 | 97.5 |
| 9 | 181.6 | 262.2 | 9 | 109.6 |
| 10 | 107.1 | 387 | 42.5 | 138.2 |
| 11 | 64.5 | 151.7 | 43 | 131.8 |
| 12 | 140 | 342 | 15.6 | 69.1 |
| 13 | 119.5 | 322 | 28.1 | 134.2 |
| 14 | 145.7 | 309 | 14 | 80.0 |
| 15 | 170.7 | 376.8 | 11 | 62.5 |

$$I_{xy} = \frac{5\sqrt{3}}{16} a^4 \tag{2}$$

$$m = \frac{3\sqrt{3}}{2} a^2 \rho \tag{3}$$

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:

$$f = \frac{\beta^2 a}{4\pi L^2} \sqrt{\frac{5E_{xy}}{6\rho}} \tag{4}$$

$$E_{xy} = \frac{96\pi^2 \rho L^4 f^2}{5\beta^4 a^2}. \tag{5}$$

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 ∼106 GPa, which is about 2–3 times larger than that of either the ZnO nanobelts [10] or the small size nanowires [19], but

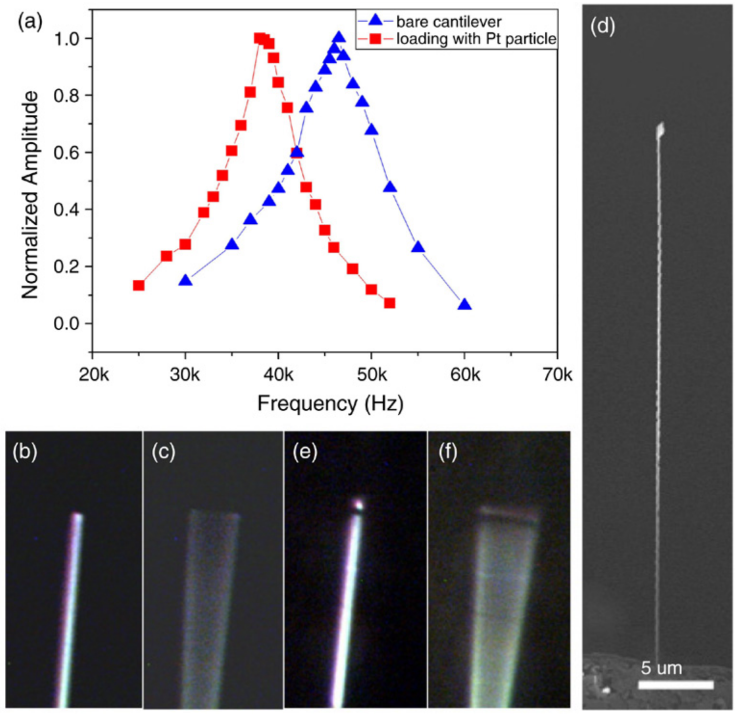


Fig. 4. (a) Frequency response plots of a cantilever before and after attaching a Pt particle at its tip, respectively; Optical microscopy images of the native ZnO nanowire cantilever at (b) stationary (c) the first harmonic resonance; (d) SEM image of the cantilever with a Pt particle at its tip, and the corresponding optical microscopy images of the loaded cantilever at (e) stationary and (f) the first harmonic resonance.

in the range of early reported results for thin films [20]. The nanowire used here grows along [0001], while the nanobelt measured previously along $[01\bar{1}0]$ or $[2\bar{1}\bar{1}0]$; 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 μm 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 ~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 μm, width 373 nm and thickness 1.75 μm. 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 ~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]

$$M_{\mathrm{eff}} = \frac{3M_0}{\beta^4}\left[\left(\frac{f_0}{f}\right)^2 - 1\right] \tag{6}$$

where $M_{\mathrm{eff}} = M_p\,(x/l)$ 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 $x = l$:

$$\frac{\Delta M_p}{M_0} \approx -\frac{6}{\beta^4}\frac{\Delta f}{f}. \tag{7}$$

From Fig. 2(b), the accuracy for measuring the frequency shift is ~0.5 kHz. At $f = 40$ kHz and for the first harmonic mode, $\Delta M_p \approx 0.006 M_0$. 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

Z.L. Wang thanks the support from NSF, the NASA Vehicle Systems Program and Department of Defense Research and Engineering (DDR&E), and the Defense Advanced Research Projects Agency (Award No. N66001-04-1-8903). NSX and S.Z. Deng thank the support of the project from the National Natural Science Foundation of China, the Ministry of Science and Technology of China, the Education Ministry of China, the Department of Education and Department of Science and Technology of Guangdong Province and Department of Science and Technology of Guangzhou City. J. Zhou thanks the KAISI FUND from SunYat-Sen (Zhongshan) University.


## References


[1] S. Frank, P. Poncharal, Z.L. Wang, W.A. De Heer, Science 280 (1998) 1744.
[2] Z. Yao, H.W.C. Postma, L. Balents, C. Dekker, Nature 402 (1999) 273.
[3] V. Derycke, R. Martel, J. Appenzeller, P. Avouris, Nano Lett. 1 (2001) 453.
[4] Y. Cui, C.M. Lieber, Science 291 (2001) 851.
[5] X. Duan, Y. Huang, Y. Cui, J. Wang, C.M. Lieber, Nature 409 (2001) 66.
[6] Z.W. Pan, Z.R. Dai, Z.L. Wang, Science 291 (2001) 1947.
[7] W.L. Hughes, Z.L. Wang, Appl. Phys. Lett. 82 (2003) 2886.
[8] P. Poncharal, Z.L. Wang, D. Ugarte, W.A. De Heer, Science 283 (1999) 1513.
[9] R.P. Gao, Z.L. Wang, Z.G. Bai, W.A. De Heer, L.M. Dai, M. Gao, Phys. Rev. Lett. 855 (2000) 622.
[10] X.D. Bai, P.X. Gao, Z.L. Wang, E.G. Wang, Appl. Phys. Lett. 82 (2003) 4806.
[11] M.F. Yu, O. Lourie, M.J. Dyer, K. Moloni, T.F. Kelly, R.S. Ruoff, Science 287 (2000) 637.
[12] B. Llic, Y. Yang, K. Aubin, R. Reichenbach, S. Krylov, H.G. Craighead, Nano Lett. 5 (2005) 925.
[13] M. Nishio, S. Sawaya, S. Akita, Appl. Phys. Lett. 86 (2005) 133111.
[14] K. Yum, Z.Y. Wang, A.P. Suryavanshi, M.F. Yu, J. Appl. Phys. 96 (2004) 3933.
[15] A. Gupta, D. Akin, R. Bashir, Appl. Phys. Lett. 84 (2004) 1976.
[16] B. Llic, D. Czaplewski, H.G. Craighead, P. Neuzil, C. Campagnolo, C. Batt, Appl. Phys. Lett. 77 (2000) 450.
[17] R.B. Bhiladvala, Z.J. Wang, Phys. Rev. E 69 (2004) 36307.
[18] L. Meirovich, Elements of Vibration Analysis, McGraw-Hill, New York, 1986.
[19] J.H. Song, X.D. Wang, E. Riedo, Z.L. Wang, Nano. Lett. 5 (2005) 1954.
[20] G. Carlotti, G. Socino, A. Petri, E. Verona, Appl. Phys. Lett. 51 (1987) 1889.
[21] W.T. Thomson, Theory of Vibration with Applications, Prentice Hall, New Jersey, 1998.
[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:

$$f_0^2 = \frac{\beta^4}{4\pi^2}\left(\frac{EI}{M_0 l^3}\right)$$

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

$$f_1^2 = \frac{3EI}{M_{\text{eff}} l^3}$$

where $M_{\text{eff}} = M_p(x/l)$ 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

$$f^2 = \frac{f_0^2 f_1^2}{f_0^2 + f_1^2} = \frac{3f_0^2}{\frac{\beta^4 M_{\text{eff}}}{M_0} + 3}.$$

Thus the effective mass $M_{\text{eff}}$ of the particle is given by

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