Detection of the Au thin-layer in the Hz per picogram regime based on the microcantilevers

Dong Won Chun\textsuperscript{a,b}, Kyo Seon Hwang\textsuperscript{a}, Kilho Eom\textsuperscript{a}, Jeong Hoon Lee\textsuperscript{c}, Byung Hak Cha\textsuperscript{a}, Woo Young Lee\textsuperscript{b}, Dae Sung Yoon\textsuperscript{a,*}, Tae Song Kim\textsuperscript{a,**}

\textsuperscript{a} Microsystem Research Center, Korea Institute of Science and Technology (KIST), 39-1 Haewolgog-dong, Seongbuk-gu, Seoul 136-761, Republic of Korea
\textsuperscript{b} Department of Materials Science and Engineering, Yonsei University, 134 Sinchon-dong, Sedaemun-gu, Seoul 120-749, Republic of Korea
\textsuperscript{c} MIT Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

Received 29 May 2006; received in revised form 14 September 2006; accepted 22 September 2006

Abstract

Through the use of oscillating microcantilevers, a micromechanical mass detection with a resolution of a Hz per picogram regime is reported. Through MEMS processes, piezoelectric microcantilevers that are simultaneously capable of self-actuation and the electrical measurement of resonant frequencies were fabricated. Mass detection in the Hz per picogram regime is demonstrated with a deposition of an Au thin-layer, of which the thickness is precisely controlled. In addition, it is shown that a scaling down of the microcantilevers enhances the sensitivity during the micromechanical mass detection.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Microcantilever; Micromechanical mass detection; Analytical sensitivity; Resonant frequency

1. Introduction

Microcantilevers have played an important role in both MEMS and bio-MEMS. In particular, recent studies suggest that microcantilevers have a great potential as biosensors for the label-free detection of biomolecules related to specific diseases [1,2]. The microcantilevers allow a label-free detection of biomolecules such as prostate specific antigen (PSA) or myoglobin by measuring the deflection change and/or resonant frequency shift driven by biomolecular interactions on the microcantilever surface [1,3,4]. Furthermore, the microcantilever can be used as a nanomechanical sensor for detecting nanoparticles [5,6] and/or a molecular layer [7–10] by measuring the deflection change and/or resonant frequency shift induced by the adsorption of the molecular layer on the microcantilever surface.

The principle for a label-free detection with microcantilevers is that the molecular adsorption on the microcantilever surface generates a flexural rigidity change and also affects the mass of a microcantilever so as to alter the deflection and/or the resonant frequency. Static-mode microcantilevers are capable of a label-free detection by measuring static deflection, while oscillating microcantilevers utilize the resonant frequency shift for a label-free detection. For static-mode microcantilevers [1,3,11], an optical apparatus is required to measure the deflection, causing difficulty in miniaturization. Further, if the deflection due to molecular adsorption is exceedingly small, difficulties may arise while measuring the deflection change at a low biomolecule concentration with the optical apparatus. For conventional oscillating microcantilevers, required is an external actuator, thus miniaturization is not likely possible. However, a recent work by the authors investigated oscillating piezoelectric microcantilevers that did not require an external actuator or optical apparatus. Consequently, the microcantilevers developed in that study may be more appropriate for miniaturized sensor applications [12–14]. In particular, these microcantilevers employ piezoelectric and converse piezoelectric effects, enabling self-actuation and an electric measurement of the resonant frequencies.

* Corresponding author. Tel.: +82 2 958 6944; fax: +82 2 958 6910.
** Corresponding author. Tel.: +82 2 958 5564; fax: +82 2 958 6910.
E-mail addresses: dsyoon@kist.re.kr (D.S. Yoon), tskim@kist.re.kr (T.S. Kim).

0924-4247/S – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.sna.2006.09.013

Recently, several cases of biomolecule detections using a piezoelectric cantilever have been reported. Biomolecule detection was accomplished by monitoring the resonant frequency shift of a piezoelectric cantilever over time. In a biomolecular interaction, the resonant frequency shift was mainly affected by the induced surface stress due to the electrostatic interaction between biomolecules. Herein, the mass contribution to the resonant frequency shift was minimized, as the mass of the reacted biomolecule monolayer on the cantilever surface was negligible. Another possible application of the piezoelectric cantilever is as a mass sensor that is similar to quartz crystal microbalance (QCM), for instance, a cantilever sensor to monitor thin film deposition. Lee et al. [15] reported that a resonant frequency shift during the deposition of an Au thin film was mainly affected by the Au mass. Accordingly, a piezoelectric cantilever is seemingly viable as a mass sensor to monitor thin film deposition in a wide thickness range.

In this article, a mass detection with a sensitivity rating of an order of 1 Hz/pg is reported using piezoelectric microcantilevers. Very small piezoelectric cantilevers with different sizes were fabricated through a MEMS processes. Through a deposition of an Au thin-layer as a mass source, the mass sensitivity of each cantilever was measured. From the experimental results, the effect of the cantilever length in 10 μm orders on the mass sensitivity is discussed.

2. Theory

The dynamic response of a microcantilever is well characterized by the following equation of motion.

$$\xi \frac{\partial^4 w(x, t)}{\partial x^4} + \mu \frac{\partial^2 w(x, t)}{\partial t^2} = 0$$

(1)

Here, $w(x, t)$ is the deflection, $\xi$ the effective bending modulus and $\mu$ is the effective mass per unit length for a microcantilever. It is noted that the effective mass per unit length, $\mu$, can be easily estimated by the rule of mixture [16,17], whereas the elasticity theory [18] enables the evaluation of the effective bending modulus $\xi$ for a microcantilever consisting of multiple layers (Fig. 1, Table 1), such as of Ta/Pt/PZT/Pt/SiO₂ for self-actuation, and electrical sensing such as $\xi = \sum E_k I_k$, where $N$ is the total number of layers (i.e. $N=5$), $E_k$ Young’s modulus for the $k$-th layer, and $I_k$ is the moment of inertia for the $k$-th layer. An analytical solution for Eq. (1) provides the resonant frequencies $f_i$ of the microcantilevers.

$$f_i = \frac{1}{2\pi} \left( \frac{\lambda_i}{l} \right)^2 \sqrt{\frac{\xi}{\mu}}$$

(2)

where $l$ is the cantilever length, and $\lambda_i$ represents eigenvalues satisfying the transcendental equation of $\cos \lambda_i \cosh \lambda_i + 1 = 0$.

In a case in which a molecular mono-layer is adsorbed on the microcantilever surface, it is assumed that molecular adsorption onto the microcantilever surface does not induce intermolecular interactions that alter the dynamic response of the microcantilevers, and that the molecular adsorption does not change the flexural rigidity of the microcantilever. The resonant frequency after the molecular adsorption is

$$f_i = \frac{1}{2\pi} \left( \frac{\lambda^*}{l} \right)^2 \sqrt{\frac{\xi}{\mu + \Delta \mu}}$$

(3)

where $\Delta \mu$ is the added mass per unit length for a molecular layer (i.e. the total mass of the molecular layer is $\Delta m = l \Delta \mu$). From Eqs. (2) and (3), the induced mass $\Delta m$ of a molecular layer is

$$\Delta m = \frac{\lambda^*}{4\pi^2 l^2} \left( \frac{1}{f^2_i} - \frac{1}{f^2_i} \right)$$

(4)

Eq. (4) allows the evaluation of the mass of the molecular layer adsorbed onto the surface by measuring the resonant frequency before and after the molecular adsorption on the surface.

For the adsorption of a minute molecular layer on a surface, i.e. $\Delta \mu \ll \mu$, the resonant frequency shift due to the adsorption

![Figure 1: Schematics of (a) a PZT microcantilever and (b) a cross-sectional view of the PZT microcantilever. The line AA' represents the neutral axis.](image)

Table 1 Parameters of the PZT microcantilever layers composed of SiNₓ/Pt/PZT/Pt/SiO₂

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness, $h$ (x 10⁻⁹) [m]</th>
<th>Thickness ratio</th>
<th>Young’s modulus, $E$ (x 10¹⁰) [N/m²]</th>
<th>Density, $\rho$ [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>200</td>
<td>0.16</td>
<td>7.30</td>
<td>2500</td>
</tr>
<tr>
<td>PZT</td>
<td>500</td>
<td>0.40</td>
<td>7.70</td>
<td>21400</td>
</tr>
<tr>
<td>Pt</td>
<td>250</td>
<td>0.20</td>
<td>16.80</td>
<td>7500</td>
</tr>
<tr>
<td>SiNₓ</td>
<td>700</td>
<td>0.24</td>
<td>29.00</td>
<td>3100</td>
</tr>
</tbody>
</table>

on the surface is approximated as follows:

$$\Delta f_i \equiv f_i - \bar{f}_i = -\frac{1}{2} f_i \frac{\Delta \mu}{\mu} = -\frac{1}{2} f_i \frac{\Delta m}{m}$$

(5)

The resonant frequency shift with respect to the loaded mass is

$$\frac{\Delta f_i}{\Delta m} = -\frac{1}{2} f_i m = -\frac{\lambda_i^2}{4\pi} \frac{1}{b h^3} \frac{E}{\rho}$$

(6)

Here, $\rho$ is the effective density, i.e. $\rho = \mu / bh$, where $b$ is the width and $h$ is the thickness. $E$ is the effective Young’s modulus defined as $E = \xi / bh^3$. Eq. (6) provides that the mass sensitivity $\Delta f / \Delta m$ is inversely proportional to $bh^3$.

3. Experimental procedure

3.1. Fabrication of the self-actuating microcantilevers

We fabricated the piezoelectric microcantilevers, consisting of multi-layers of Ta/Pt/PZT/Pt/SiO$_2$ on a SiN$_x$ supporting layer, for electrical self-actuating and sensing without any external oscillators or an optical apparatus. Fig. 2 shows the fabrication process of the PZT microcantilever. For the piezoelectric capacitor, p-doped Si (1 0 0) wafer (525 ± 20 μm thickness) substrates with a 100 mm-diameter were utilized for the deposition of low-stress 0.7 μm silicon nitride (SiN$_x$) layers using low-pressure chemical vapor deposition (LPCVD). A Ta layer with a thickness of 0.03 μm allowed a bottom electrode layer (Pt layer) with a thickness of 0.15 μm to be bound to the SiN$_x$ layer. The PZT films were deposited on the bottom electrode by the spin coating of a mixed PZT solution (diol-based sol–gel route) at 3000 rpm for 30 s. They were subsequently fired at 400 °C for 5 min and then annealed at 650 °C for 10 min. For a metal-ferroelectric-metal (MFM) capacitor structure, a Pt layer was deposited onto a PZT film as a top electrode via RF sputtering. The Pt layer as a top electrode in addition to the PZT layer was etched by inductive coupled plasma (ICP) etching. A SiO$_2$ thin film with a thickness of 0.2 μm was deposited onto the top electrode via a plasma-enhanced chemical vapor deposition (PECVD) process. Following this, contact holes on the top electrode were etched. The contact electrode and the top electrode were connected through an Au lift-off process. The pattern of the Pt bottom electrode was conducted with ICP, while the pattern of the bottom SiN$_x$ window was done by reactive ion etching (RIE). The bulk silicon (p-doped Si wafer) was then etched using KOH. Finally, the etching of the SiN$_x$ layer (top SiN$_x$ layer on Si wafer) was implemented via RIE. After the fabrication of the piezoelectric microcantilever, a SiO$_2$ thin film with thickness of 1000 Å was deposited by means of PECVD as an electrical, chemical passivation layer. Fig. 3 shows an SEM image of piezoelectric microcantilevers with the varying dimen-
sions of 15 μm × 60 μm, 15 μm × 50 μm, and 15 μm × 35 μm (width × length).

3.2. Measuring the resonant frequency shift due to induced mass of the gold layer

In order to measure the resonant frequency of the microcantilevers, we used an impedance analyzer (4292A, Agilent technologies, USA), which enabled the monitoring of the phase angle as a function of the sweeping frequency. Specifically, while the phase angle of the impedance for a microcantilever that functions as a capacitor is approximately −90° in the off-resonance, the phase angle in the resonant frequency exhibits the peak value that is responsible for the microcantilever motion.

The resonant frequency shift induced by the mass of the Au was measured using an impedance analyzer. The resonant frequencies of the microcantilever were measured before and after the deposition of the Au layer, and the resonant frequency shift was then calculated. The Au thin-layer was deposited on the microcantilever with thicknesses of 6, 12, 32, and 50 Å using the thermal evaporator. The thickness of the Au layer was precisely controlled by a thickness/rate monitor system (Sycon Instruments, USA), which was a component of the thermal evaporator. From these measured resonant frequencies, it was possible to estimate the resonant frequency shift induced by the Au layer.

4. Result

4.1. Dynamic behavior of the microcantilevers based on the length scale

As stated earlier, the impedance analyzer enables the measurement of the resonant frequency of microcantilevers. Fig. 4 shows the phase angle change as a function of the sweeping frequency of the proposed fabricated microcantilever with a dimension of 20 μm × 80 μm. At off-resonance, the phase angle is not quite −90° due to parasitic impedance generated by the cable and the probe connecting the electrode of the cantilever to the impedance analyzer. However, the phase angle shift in the resonance was much larger than phase angle shift originated from the parasitic impedance, thus the parasitic impedance is negligible in the measurement of the resonance frequency.

In Fig. 5, it is shown that the size effect plays a role on the dynamic response of microcantilevers. Specifically, the length scale plays a vital role on the dynamic response, whereas the width scale does not affect the dynamic response. This is consistent with the theoretical model in which the resonant frequency is dependent only on the length. That is, the resonant frequency is inversely proportional to the square of the length, as suggested in Eq. (2). The experimental data for resonant frequencies of microcantilevers with a length scale larger than 50 μm are quantitatively identical to the theoretical predictions, whereas for microcantilevers with a length scale less than 50 μm, the theoretical model does not allow a precise prediction of the resonant frequencies (see Fig. 5). Furthermore, the deviation of the experimental data for the resonant frequency from the theoretical model becomes larger as the length scale of the microcantilevers becomes smaller. The difference between the experimental data and the analytical predictions can be ascribed to the etching fabrication process, which can affect the SiN₃ supporting layer. That is, for a small length scale that increases the resonant frequency enormously, the effect of the etching fabrication that changes the thickness and flexural rigidity may induce a significant deviation of the resonant frequency obtained by experiments from the analytical expectations. Moreover, deviation of the measured resonant frequency from theoretical predictions can be attributed to the photolithography fabrication process. During this process, corners of the mask-defined patterns are exposed to undesired scattered light whereas several areas outside the mask-defined pattern, especially the anchors of the cantilever, are exposed to a smaller amount of light compared to the other non-masked area. These circumstances result from the diffraction/scattering of the incident UV-light near the corners or anchors of the pattern. Accordingly, the photoresist around the corners and anchors are not perfectly developed, leading to a reduction of pattern fidelity [19]. As the cantilever dimension becomes smaller, this effect leads to a more severe alteration of the dimension of the
Table 2

<table>
<thead>
<tr>
<th>Au thickness (Å)</th>
<th>Loaded mass (pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 μm × 80 μm</td>
</tr>
<tr>
<td>6</td>
<td>18.58</td>
</tr>
<tr>
<td>18</td>
<td>55.58</td>
</tr>
<tr>
<td>50</td>
<td>154.4</td>
</tr>
<tr>
<td>100</td>
<td>308.8</td>
</tr>
</tbody>
</table>

The dynamic response change of microcantilevers is quantitatively similar to the theoretical predictions. The mass sensitivity of the microcantilever with a dimension of 10 μm × 30 μm, 15 μm × 60 μm, and 10 μm × 30 μm, respectively. For the microcantilever with a dimension of 10 μm × 30 μm, the experimental data of the resonant frequency shift from Eq. (6), on the mass sensitivity is 76.92 Hz/pg.

As suggested in the theory, the mass sensitivity $\Delta f/\Delta m$ is related to the width and the length such as $\Delta f/\Delta m \sim 1/b^3$. Here, the mass sensitivity $\Delta f/\Delta m$ is denoted as $\alpha$, i.e., $\alpha = \Delta f/\Delta m$. Two microcantilevers are considered, for example, Cantilever (1) and Cantilever (2). From Eq. (6), the ratio of the mass sensitivity between the two microcantilevers is given as

$$\frac{\alpha^{(2)}}{\alpha^{(1)}} = \left[ \frac{b^{(2)}}{b^{(1)}} \right] \left[ \frac{l^{(2)}}{l^{(1)}} \right]^3$$

(9)

Here, the superscript $(i)$ indicates the microcantilever $(i)$, where $i = 1, 2$. Taken into account are the two microcantilevers whose dimensions are 10 μm × 30 μm [Cantilever (1)] and 15 μm × 60 μm [Cantilever (2)]. From the experiments, the ratio of the mass sensitivity is $\alpha^{(2)}/\alpha^{(1)} = 0.1025$, while the theoretical prediction from Eq. (9) results in the ratio of the mass sensitivity of $\alpha^{(2)}/\alpha^{(1)} = 0.08333$. This indicates that the mass sensitivity obeys the rule that $\Delta f/\Delta m$ is inversely proportional to $b^3$.

5. Conclusion

In this article, microcantilevers that can detect the induced mass of an Au thin film layer in the order of 1 Hz/pg are reported. This study shows that the scaling down of the microcantilever significantly increases the mass sensitivity. Specifically, it is shown that the mass sensitivity is related to the width and the length, given as Eq. (6). This relationship suggests that small length-scale microcantilevers are appropriate for the monitoring of depositions of thin films with a high mass sensitivity. That is, microcantilevers operated in vibration (oscillation) mode enable the possibility of miniaturization, while simultaneously enhancing mass sensitivity. Thus, these self-actuating microcantilevers exhibit a high potential for utilization as sensors and/or biosensors.

Acknowledgments

The authors are very grateful for the financial support from the Intelligent Microsystem Center sponsored by the Korea Ministry of Science and Technology as a part of the Twenty-first Century Frontiers R&D Project (Grant MS-01-133-01), and from the National Core Research Center for Nanomedical Technology sponsored by KOSEF (Grant R15-2004-024-00000-0). D.W.C. would like to appreciate Dr. Jongin Hong (Korea Institute of Science and Technology) and WooYoung Shim and DoHun Kim (Yonsei University) for helpful discussions.
References

Bioassembly of prostate-specific antigen (PSA) using microcantilevers, Nat.

Guntherodt, Ch. Gerber, J.K. Gimzewski, Translation biomolecular recognition

Meyer, M. Hegner, C. Gerber, Label-free protein assay based on a nanome-

tative analysis of a prostate-specific antigen (psa) using a nanomechanical

chanical detection of the specific activities of endonucleases by cantilevers,

se-based logic gates and sensors using magnetic force-amplified readout of

H. Güntherodt, Surface stress in the self-assembly of alkane thiols on gold,

Mechanical resonant immunospecific biological detector, Appl. Phys. Lett.

[9] B. Ilic, Y. Yang, H.G. Craighead, Virus detection using nanoelectome-

sensor for discerning biomolecular interaction, Anal. Chem. 77 (2005)
1601–1606.

Chakraborty, A. Majumdar, Origin of nanomechanical cantilever movement

free novel electrical detection using micromachined pzt monolithic thin film
cantilever for the detection of C-reactive protein, Biosens. Bioelectro.

say of prostate-specific antigen (PSA) using resonant frequency shift of piezo-
electric nanomechanical microcantilever, Biosens. Bioelectro. 20

frequency shift of functionalized Pb(Zr0.52Ti0.48)O3 thin film microcan-
tilever for the detection of C-reactive protein, Appl. Phys. Lett. 84 (2004)
5318–5319.

sensitivity using micromachined PZT cantilever, Integr. Ferroelectro.

behavior of ceramic bending mode actuators under strong electric fields, J.

[17] Q.-M. Wang, L.E. Cross, Determination of Young’s modulus of the reduced
5358–5363.

Beemom CC, pp. 300–311.


Biographies

Dong Won Chun was born in 1978 in Seoul, South-Korea. He received the
BS degree in Department of Materials Science and Engineering from the Yon-
sei University, Seoul, where he is currently working toward the MS degree in
Department of Materials Science and Engineering. He is interested in MEMS,
nanomechanics, MEMS sensor and integrated micro/nano device.

Kyo Seon Hwang was born in Seoul, on January 31, 1980. He received the BS
and MS degrees in electronics and computer engineering, in 2002 and 2004,
respectively, from Korea University, Seoul, where he is currently working
at the PhD degree in electronics and computer engineering. He is student researcher
with the Korea Institute of Science and Technology, Seoul. His research interests
include BioMEMS, nanomechanics, integrated micro/nano device.

Kihlo Eom earned PhD degree in Department of Aerospace Engineering &
Engineering Mechanics (ASEEM) in the University of Texas at Austin (UT Austin).
During his PhD works (2000–2005), his research regarding coarse-
grained modeling of proteins was supported by Department of ASEEM, Institute
of Computational Engineering and Science (ICES), Institute for Theoretical
Chemistry (ITC), and Department of Chemistry in UT Austin as an inter-
disciplinary research. After earning PhD degree in August 2005, he joined to Microsystem Research Center in Korea Institute of Science and Technol-
ogy (KIST) as a research scientist. He is currently involved in the research
project regarding a microcantilever-based biosensor for a label-free detection
of biomolecules. Moreover, he is also involved in the computational modeling
of protein molecules based on statistical physics theory. His current research
interest is the theoretical model study on nanomechanics of bio-MEMS and
biological macromolecules (DNA, protein).

Jeong hoon Lee is a Postdoctoral Associate at Massachusetts Institute of
Technology (MIT), USA. He is currently a member of the Micro/Nanofluidics
BioMEMS Group at Research Laboratory of Electronics (RLE). His main
research in MIT is the development of nanofluidic systems and Macro-to-
micro/nano interfaces. He received the BS and MS degrees in ceramic engineer-
ing from the Yonsei University, Seoul, Korea, in 1997, and 1999. He received his
PhD from Yonsei University in 2004. He specialized in MEMS/Nanomechanics.
From 1999 to 2005, he was a research scientist in the Microsystems Research
Center at Korea Institute of Science and Technology (KIST) in Seoul, Korea.
He is interested in the application and development of MEMS, nanomechanics, 
tegrated micro/nano devices and self assembled monolayer (SAMs) forma-
tion.

Byung Hak Cha was born in 1981 in Seoul, Korea. He received the BS degree
in Electrical engineering from Soongsil University, Seoul in 2006. He directly
entered the MS degree in Electrical engineering from Korea University, Seoul.
Since January 2006, he has been working on student researcher at Nano Bio
System Laboratory of Korea Institute of Science and Technology. His current
research focused on the fabrication of piezoelectric thin film microcantilevers
using MEMS fabrication process and the study of biosensor applications to
microcantilever.

Woo Young Lee is with Department of Materials Science and Engineering,
Yonsei University. He received BS and MS in Metallurgical Engineering from
Yonsei University in 1986 and 1988, and PhD in Physics from University of
Cambridge in 2000. In recent years, his research interests have centered on
spintronic devices, nano-bio sensors based on nanowires, and hydrogen sensors.
He has authored or co-authored over 90 publications.

Dae Sung Yoon received the BS degree in ceramic engineering from Yonsei
University, in 1991, and the PhD degree in materials science and engineering
from Korea Advanced Institute of Science and Technology, in 1996. He was a
post-doctoral associate studying nano-biosensor at Department of Materials
Science and Engineering, University of Pennsylvania, from 1999 to 2000, and
a principal research scientist studying BioMEMS and nano-biosensor at Samsung
Advanced Institute of Technology, from 1996 to 2003. He is currently a senior
research scientist at Microsystem Research Center, KIST in Seoul, His research
interests include nano-biosensor, Bio MEMS/NEMS, and bio-materials.

Tae Song Kim is Principal Research Scientist at KIST. He was awarded the
PhD and MS degree in Material Science and Engineering from Korea Advanced
Institute of Science and Technology (KAIST) in 1984 and 1993, and the Bach-
elor of Engineering with majors in Electronic Material and devices from Yonsei
University in 1982. He joined the department of electrical and computer sci-
ence engineering, University of Minnesota, USA as a post-doctoral associate
for the study of MEMS devices from 1997 to 1998. His research activities
have been focused on the BioMEMS, BioSensor/Chip and piezoelectric MEMS
devices.


ARTICLE IN PRESS
SNA-5599; No. of Pages 6