Mechanism of flexural resonance frequency shift of a piezoelectric microcantilever sensor during humidity detection

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We have examined the flexural resonance frequency shift of a piezoelectric microcantilever sensor (PEMS) during humidity detection and have shown that the flexural resonance frequency shift of the PEMS during detection was a result of Young's modulus change of its piezoelectric layer. Because of the piezoelectric layer's Young's modulus change, the PEMS flexural resonance frequency shift was more than 300 times larger than could be accounted for by mass loading. © 2008 American Institute of Physics. [DOI: 10.1063/1.2921050]

A piezoelectric microcantilever sensor (PEMS) is a sensor platform consisting of a highly piezoelectric layer bonded to a nonpiezoelectric layer whose flexural resonance peaks are used for detection.^{1–10} Microcantilevers—PEMS included—are usually thought of as a mass sensor: Binding of target analytes to the sensor surface increases the sensor's mass, which in turn decreases their flexural resonance frequency. Detection of target analytes is achieved by monitoring the resonance frequency shifts of the sensors.^{1–10} However, recent experiments indicated that PEMS flexural resonance frequency shifts during detection were more than two orders of magnitude larger than could be accounted for by the mass change alone.^{2–10} The larger than expected resonance frequency shift was attributed to PEMS effective spring constant change,^{2–4} which could be a result of the dimensional or Young's modulus change or both. Although two existing theories, one involving a taut-string analogy¹¹ and the other a buckling analogy,¹² tried to take into account the microcantilever's effective spring constant change by the binding-induced surface stress, both fail to consider the dimensional or Young's modulus change in a microcantilever. Therefore, it is still unclear what physical change is responsible for the observed large resonance frequency shifts.

A recent experiment on lead magnesium niobate-lead titanate solid solution (PMN-PT) PEMS showed that the PEMS flexural resonance frequency could be changed by a dc bias electric field (dc field, E , thereafter) as a result of Young's modulus change in the PEMS piezoelectric layer.¹³ As similar to dc fields, stresses can also cause Young's modulus of a soft piezoelectric to change.^{15,16} It is possible that a PEMS larger than the expected resonance frequency shift is also a result of Young's modulus change in its piezoelectric layer, which is perhaps due to the binding-induced stresses.

The purpose of this study is to examine whether Young's modulus of the PEMS piezoelectric layer changes during detection and whether the PEMS flexural resonance frequency shift can be accounted for by this Young's modulus change during detection. A PMN-PT/tin PEMS $900 \pm 100 \mu\text{m}$ long and $700 \pm 50 \mu\text{m}$ wide consisting of an $8 \mu\text{m}$ thick PMN-PT layer¹⁷ bonded to a $6 \mu\text{m}$ tin layer by electroplating was

subject to humidity detection.⁵ To quantify the change of Young's modulus change in the PMN-PT layer, a separate PMN-PT strip of the same thickness ($8 \mu\text{m}$), which is $700 \pm 50 \mu\text{m}$ long and $700 \pm 100 \mu\text{m}$ wide, with both major surfaces coated with gold, was also subjected to the same humidity detection. The PMN-PT PEMS had a gold surface on the PMN-PT side and a tin surface on the other side. The two dissimilar surfaces caused the PEMS to bend during humidity detection, which was measured to quantify the detection-induced strain.

The humidity detection was carried out in a sealed glovebox of 126 L (Bel-Art Products, Pequannock, NJ) with the humidity and temperature constantly monitored (VWR International, West Chester, PA). A humidifier (Sunbeam Product, Inc., Boca Raton, FL) was first connected to the glovebox to achieve a 90% relative humidity (RH). Dry air was then introduced to decrease the RH to desired levels. After a desired RH level was reached, we waited for an additional 5–10 mins. to ensure that the desorption of the water molecules was well equilibrated. The temperature inside the glovebox was $23 \pm 0.1^\circ\text{C}$ throughout all experiments. Exemplary flexural resonance spectra of the PEMS at 30% and 60% RH obtained with an Agilent 4294A impedance analyzer (Palo Alto, CA) are shown in Fig. 1(a), where the phase angle, $\theta = \tan^{-1}[\text{Im}(I)/\text{Re}(I)]$, was between the real part $\text{Re}(I)$ and the imaginary part $\text{Im}(I)$ of the complex electrical impedance I . An optical micrograph of the PEMS is shown as the insert of Fig. 1(a). By comparing the spectra at different RHs, we confirmed that the observed resonance frequency shift was a result of the desorption of the water molecules but not of the damping or peak distortion from different field values or frequency sweeping conditions. In Fig. 1(b), we plot $(\Delta f/f)_{\text{RH}}$ versus RH, where f and Δf are the resonance frequency at 60% RH and the difference of the resonance frequency at a given RH from that at 60% RH, respectively, and the subscript RH denotes that $\Delta f/f$ was due to the RH change. With the present planar detection geometry, the resonance frequency shift due to mass change can be deduced by using⁵ $(\Delta f/f)_{\text{mass}} = -\Delta m/2M$, where $\Delta m = (\Delta\Gamma_{\text{Sn}} + \Delta\Gamma_{\text{Au}})wL$ and $M = (\rho_p t_p + \rho_n t_n)wL$ are the mass change and the mass of the PEMS, respectively, with $\Delta\Gamma_{\text{Sn}}$ and $\Delta\Gamma_{\text{Au}}$ denoting the water molecule adsorption density changes on the tin surface and that on the gold surface, re-

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FIG. 1. (Color online) (a) Flexural-mode resonance spectra at 60% and 30% RH and (b) $(\Delta f/f)_{RH}$ and $-d_{RH}$ vs RH and $(\Delta f/f)_{DC}$ and d_{DC} vs E of the PMN-PT PEMS. The insert in (a) shows the top view optical micrograph of the PEMS and inserts I and II in (b), respectively, show how the PEMS bent with an increasing E and a decreasing RH. Also plotted in (b) is the $\Delta f/f$ deduced from Young's modulus change of the PMN-PT strip (solid diamonds).

spectively, w and L the PEMS width and length, respectively, and $\rho_p = 7.9 \text{ g/cm}^3$ and $t_p = 8 \text{ }\mu\text{m}$ ($\rho_n = 7.3 \text{ g/cm}^3$ and $t_n = 6 \text{ }\mu\text{m}$) the density and thickness of the PMN-PT (tin) layer, respectively. By using two 10 MHz quartz crystal microbalances (QCMs), one with two gold surfaces and the other with one tin surface and one gold surface,⁵ we deduced that from 60% to 30% RH, $\Delta\Gamma_{Sn} = -1.3$ and $\Delta\Gamma_{Au} = -0.4 \text{ ng/mm}^2$, respectively. Therefore, $(\Delta f/f)_{mass} = 8 \times 10^{-6}$, which was 300 times too small to account for the observed resonance frequency shift of 2.5×10^{-3} from 60% RH to 30% RH, as shown in Fig. 1(b).

Furthermore, because $\Delta\Gamma_{Sn}$ was around three times $\Delta\Gamma_{Au}$, the PEMS bent when the RH changed. The PEMS axial tip displacement d_{RH} was monitored *in situ* during the detection by using a LC-2450 laser displacement meter with a $0.5 \text{ }\mu\text{m}$ resolution (Keyence, Osaka, Japan), where the subscript RH denotes the RH change. Also plotted in Fig. 1(b) is $-d_{RH}$ versus RH. Note that a negative d_{RH} indicates that the PEMS bent toward the tin side [insert II of Fig. 1(b)]. From d_{RH} , we deduced that the average lateral strain^{18,19} ϵ_{ave} , was 4×10^{-5} in the PMN-PT layer, also about 60 times too small to account for the measured $(\Delta f/f)_{RH}$ shown in Fig. 1(b).

FIG. 2. (Color online) $(\Delta f/f)_{RH}$ vs RH and $(\Delta f/f)_{dc}$ vs E of a separate PMN-PT strip. The insert I is the top view optical micrograph of the strip and insert II is the width-mode resonance spectra of the PMN-PT strip at 30% and 60% RH.

This ruled out strain as a main factor for the observed resonance frequency shift.

Separately, we subjected the PEMS to a dc field and simultaneously measured the resonance frequency shift and the tip displacement d . The resultant $(\Delta f/f)_{dc}$ and d_{dc} versus E are also plotted in Fig. 1(b), where f and Δf are, respectively, the flexural resonance frequency at $E=0$ and the difference of the resonance at a given E from that at $E=0$ and the subscript dc denotes that $\Delta f/f$ and d were due to the dc field change. Note that an $E > 0$ denotes a field parallel to the poling direction of the PMN-PT layer [insert I in Fig. 1(b)]. As can be seen, for both $\Delta f/f$ and d , the effect of decreasing the RH from 60% to 30% was similar to the effect of changing E from 0 to 3 kV/cm. As both the mass loading effect and the detection-induced strain could not account for the observed $\Delta f/f$, the similarity between the effects of the RH change and that of the dc field suggests that the present humidity-change-induced $\Delta f/f$ could also be a result of Young's modulus change in the PMN-PT layer.

To examine whether Young's modulus of the PMN-PT layer changed during humidity detection, we subjected the separate PMN-PT strip in the humidity detection and monitor its fundamental width-mode resonance frequency. Width-mode resonance frequency measurement is a standard way of determining the lateral Young's modulus Y_p of a rectangular piezoelectric plate.²⁰ For easy handling, the PMN-PT strip was also in cantilever geometry. Note that the PMN-PT strip did not exhibit a flexural-mode resonance peak due to the lack of a nonpiezoelectric layer. To make sure that the lateral stress of the PMN-PT strip did not change sign across its thickness, it had two identical gold surfaces such that no bending occurred in the PMN-PT strip during humidity detection. An optical micrograph of the PMN-PT strip is shown in the Inset I of Fig. 2. The width-mode resonance spectra of the strip at various RHs are shown in the insert II of Fig. 2. Clearly, the width-mode resonance frequency of the strip shifted with a changing RH. With f and Δf as defined above, we plot $(\Delta f/f)_{RH}$ versus RH of the PMN-PT strip in Fig. 2.

Such $(\Delta f/f)_{RH}$ increased with a decreasing RH indicates that the lateral Young's modulus of the PMN-PT strip indeed changed with a changing RH. Furthermore, the $(\Delta f/f)_{RH}$ of the width mode of the PMN-PT strip was similar to that of the flexural mode of the PMN-PT PEMS in that both increased with a decreasing RH. For further comparison, we subjected the PMN-PT strip to a dc field and measured its width-mode resonance frequency shift. The resultant $(\Delta f/f)_{dc}$ versus E of the PMN-PT strip is also plotted in Fig. 2. Clearly, for the width mode of the PMN-PT strip, the effect of a positive E was also similar to that of a decreasing RH.

The width-mode resonance frequency f_w of the PMN-PT strip was related to the lateral Young's modulus Y_p , the density ρ_p , and the width w as²⁰ $f_w = (Y_p/\rho_p)^{1/2}/2w$. Because $\Delta f_w/f_w \ll 1$ and the width change was negligible, the $\Delta Y_p/Y_p$ of the strip could be readily deduced as $(\Delta Y_p/Y_p)_{strip} \cong 2(\Delta f_w/f_w)_{strip}$. Furthermore, the adsorbed density change on the tin surface was about three times that of the gold surface, and the PMN-PT strip had two gold surfaces, while the PEMS had one tin and one gold surfaces. Therefore, the PMN-PT strip absorbed only about half the amount the PEMS adsorbed. Assuming ΔY_p to be proportional to the binding-induced stress change, which in turn is proportional to the adsorbed mass density change, the relative Young's modulus change of the PMN-PT layer in the PEMS $(\Delta Y_p/Y_p)_{PEMS}$ could be approximated as $(\Delta Y_p/Y_p)_{PEMS} \cong 2(\Delta Y_p/Y_p)_{strip}$, and $(\Delta f/f)_{RH}$ of the PEMS could be deduced by using²¹ $f_f \cong (1/2\pi)\sqrt{k/0.234M}$, with $k = Y_{eff}t^3w/4L^3$ and $Y_{eff} \cong [Y_p^4 + Y_n^4 + 2Y_pY_n t_p t_n (2t_p^2 + 2t_n^2 + 3t_p t_n)]/(Y_p t_p + Y_n t_n)(t_p + t_n)^3$ being the effective spring constant and the effective Young's modulus of the PEMS, respectively, where $Y_n = 50$ GPa, $Y_p = Y_{p,0} + \Delta Y_p = Y_{p,0}[1 + (\Delta Y_p/Y_p)_{PEMS}]$ with $Y_{p,0} = 80$ GPa. The deduced $\Delta f/f$ versus RH of the PEMS is also plotted in Fig. 1(b). Clearly, the deduced $\Delta f/f$ versus RH of the PMN-PT PEMS using the Young's modulus change obtained from the PMN-PT strip overlapped with experimental results within the experimental uncertainty, validating that Young's modulus change was indeed the underlying mechanism for the PEMS flexural-mode resonance frequency shift during humidity detection.

To further compare the $\Delta f/f$ of the PMN-PT PEMS observed in the humidity detection to the $\Delta f/f$ obtained with a dc bias field, we replot the results shown in Fig. 1(b) as $(\Delta f/f)_{RH}$ versus $-\varepsilon_{ave,RH}$ and $(\Delta f/f)_{dc}$ versus $\varepsilon_{ave,dc}$ in Fig. 3, where $\varepsilon_{ave,RH}$ and $\varepsilon_{ave,dc}$ were the average bending strains of the PMN-PT layer as deduced from the axial displacement,¹⁹ $-d_{RH}$ and d_{DC} shown in Fig. 1(b), respectively. Clearly, $\Delta f/f$ of the PMN-PT PEMS correlated well with the lateral strains of the PMN-PT layer in both humidity detection and in a dc field, further confirming that the flexural $\Delta f/f$ in the present PEMS was a result of Young's modulus change in the PMN-PT layer. In the dc field, the underlying mechanism for Young's modulus change is the non-180° polarization domain switching.¹³ Through the comparisons in Figs. 1–3, we believe that Young's modulus change in the present humidity detection was also due to polarization domain switching due to binding-induced stress.¹⁴

In summary, we have shown that the flexural resonance frequency shift of a PEMS during humidity detection was due to Young's modulus change of its piezoelectric layer,

FIG. 3. (Color online) $(\Delta f/f)_{RH}$ and $(\Delta Y_p/Y_p)_{RH}$ vs $-\varepsilon_{ave,RH}$ and $(\Delta f/f)_{dc}$ and $(\Delta Y_p/Y_p)_{dc}$ vs $\varepsilon_{ave,dc}$, where $(\Delta f/f)_{RH}$ and $(\Delta f/f)_{dc}$ are replotted from Fig. 1(b) and $-\varepsilon_{ave,RH}$ and $\varepsilon_{ave,dc}$ are the average bending strains and $(\Delta Y_p/Y_p)_{RH}$ and $(\Delta Y_p/Y_p)_{dc}$ are the relative Young's modulus changes in the PMN-PT layer of the PEMS as deduced from the axial displacement shown in Fig. 1(b) and from the relative resonance frequency shift of the PEMS, respectively. The dashed line is to guide the eye.

which was 300 times larger than could be accounted for by the mass loading alone. Furthermore, because of Young's modulus change during detection, the use of Stoney's equation would exaggerate the surface stress by two orders of magnitude.

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