Moisture measurement using porous aluminum oxide coated microcantilevers

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1. Introduction

Current techniques to measure low-level water vapor content include cooled (chilled) mirrors, electrolytic cells, oscillating crystals, infrared absorption, metal oxide or polymer capacitive films, etc. [1,2]. The prices range from a couple of thousand to tens of thousands US dollars. Besides these devices, length-of-stain tubes include cooled (chilled) mirrors, electrolytic cells, oscillating crys-
tals, other devices are less sensitive than optical devices, but more cost-effective. The disadvantages of all these practical moisture measurement systems demand a sensor which withstands corrosive and contaminating gases since these devices do not directly contact with gases. In general, other devices are less sensitive than optical devices, but more cost-effective. The disadvantages of all these practical moisture measurement systems demand a sensor which withstands corrosive and contaminating gases, a sensor which is sensitive enough to sudden and drastic changes of moisture, and a sensor which has a higher calibrated life period.

Advances in the field of micro-electro-mechanical systems (MEMS) now offer unique opportunities to design sensitive and cost-effective analytical methods. Recently, microcantilevers (MCLs) have been proven to be an attractive platform for sensors with on-chip electronic circuitry and extreme sensitivity [3,4]. Because the micromechanical aspects of the MCL can be integrated with on-chip electronic circuitry, it provided an outstanding platform for chemical [5,6] and biological sensors [7,8]. Extremely sensitive chemical vapor sensors based on MCLs have been demonstrated using selective coatings on the MCLs.

Two characteristics of a microcantilever, the deflection and resonance frequency, can be used to detect chemicals. MCLs operating in the dynamic mode, i.e., resonance frequency mode, are essentially mechanical oscillators. From the simple classical models such as simple harmonic motion, the frequency of an oscillating MCL, \( f \), can be given in equation

\[
f = \frac{1}{2\pi} \times \sqrt{\frac{k}{m^*}},
\]

where \( k \) is the spring constant and \( m^* \) is the effective mass of the cantilever [9,10].

The three main factors that affect the change of resonating frequency of the cantilever are adsorption-induced mass loading, viscosity of the media induced damping, and environment-induced
elasticity changes in MCL materials. In many sensing applications, the frequency changes due to viscosity of the medium, and elasticity changes of the material of the MCLs are insignificant when operated in air. Hence, the analyte mass binding to the MCL can be related to a shift in the MCL resonance frequency from initial frequency, $f_0$, to final frequency, $f_1$, as expressed in equation.

$$\Delta m = \frac{k}{4\pi^2} \left[ \frac{1}{f_1^2} - \frac{1}{f_0^2} \right].$$

where $\Delta m$ is the additional mass.

The static mode, i.e., the deflection mode, was widely used in studies of MCL sensors. MCLs undergo bending due to molecular adsorption by confining the adsorption to one side of the cantilever. Adsorption or intercalation of the analyte will markedly change the surface characteristics of the MCL, and results in the bending of the MCL. Using Stoney’s formula [11], the deflection at the end of a MCL, $\Delta Z$, due to adsorption can be written as:

$$\Delta Z = \frac{3(1 - \nu)E_l^2}{2(1 + \nu)(1 - 2\nu)} \frac{\Delta s}{Z},$$

where $\nu$ and $E$ are Poisson’s ratio and Young’s modulus for the substrate, respectively, $L$ is the length of the cantilever, $t$ is the thickness of the MCL, and $\Delta s$ is the surface stress.

MCL-based moisture sensors have been developed using SiO$_2$, Si$_3$N$_4$, and polymer coatings [12–15]. However, these sensors are not sensitive enough for ppm level moisture detection. Aluminum oxide (Al$_2$O$_3$), on the other hand, has been demonstrated highly selective for moisture measurement [16–18] and an excellent material for measurement of moisture in most industrial gases. Recently, we reported that Al$_2$O$_3$ film modified MCLs can be used for sensitive detection of moisture [19]. The Al$_2$O$_3$ film was prepared by thermal oxidation of Al on the MCLs. The adsorption of water molecules on the thin film resulted in the surface stress on the Al$_2$O$_3$ film that deflected the MCL. The sensitivity, temperature effects, and selectivity of the Al$_2$O$_3$-modified MCLs for low-level moisture detection have been discussed. The moisture detection limit was 10 ppm using the deflection mode, but the frequency change of the MCLs was not investigated. The sensitivity could be further improved by fine tuning of the coatings.

It was now well-known that the surface characteristic of the coatings is critical for the MCL sensing performance. Increasing surface area is a practical approach for enhancing sensitivity of MCL sensors. For moisture measurement, it is anticipated the porous Al$_2$O$_3$-modified MCLs will have better sensitivity than our previous reported ones. The nano-porous film was developed by an anodization method so called anodization process. Aluminum when anodized in basic or acidic solution with a suitable applied potential and time would be converted into porous aluminum oxide [20]. In this paper, we compare the sensitivity for moisture measurement of MCLs modified by the anodized porous aluminum oxide and aluminum oxide prepared by thermal oxidation of aluminum. Both dynamic and static modes were investigated.

2. Experimental

2.1. Materials

In our experiments, we used commercially available silicon MCLs (Veeco Instruments, Santa Barbara, CA). The dimensions of the V-shaped silicon MCLs were 180 $\mu$m in length, 25 $\mu$m in leg width, and 1 $\mu$m in thickness. Both sides of these MCLs were originally covered with a thin film of chromium (3 nm) and followed by a 20-nm layer of gold, both deposited by e-beam evaporation. One side of MCL was then deposited by a layer of 500-nm-thick aluminum (Al). The Al films were oxidized to Al$_2$O$_3$ using two different methods. For Method I, the Al film was oxidized by oxygen in a high vacuum chamber while oxygen gas was flowing through at 100 °C. A SEM picture of the thermal oxidized Al$_2$O$_3$ coating was shown in Fig. 1A. For Method II, aluminum was converted to nano-porous aluminum oxide by an anodization process [21]. The aluminum on the MCLs was anodized in a 0.1 M oxalic acid solution with a voltage of 40 V and a current density of 0.5 mA/cm$^2$ for 8 min. This condition was applied to generate pores at smaller diameter for larger adsorption capacity. The Al-coated MCL was used as the anode and a Pt wire was used as the cathode. The aluminum films with thickness varied from 100 to 500 nm were investigated to study the thickness effects on sensor sensitivity. However, only aluminum with a 500 nm thickness was found effective in producing pores, and no porous Al$_2$O$_3$ were formed from the aluminum films with the thickness of 100, 200, and 300 nm. Fig. 1 is a SEM image of the porous Al$_2$O$_3$ film with 500 nm in thickness on a MCL after the anodization process. After anodization, the thickness of the Al$_2$O$_3$ decreased to 125 nm. The pores were clearly seen on the aluminum grains. The average diameter of the pores was approximately 7 nm. Because of the Al$_2$O$_3$ layer was relatively thin, we used the same Young’s modulus and spring constant of the silicon cantilevers for a simplified calculation although errors are expected.
2.2. Gas system

Dry nitrogen was used as the carrier gas for sensing validation. Dry nitrogen was passed through a gas bubbler containing distilled water used to generate wet gas. Dual stage gas regulators for wet and dry gases controlled the gas flow into a gas mixing setup. The desired moisture level was obtained by controlled mixing of the dry and wet gases. The magnetic heater and thermometer as well as a water bath provided the temperature control of the vapor generation system at 25 °C. The moisture level of the final mixture was measured using a Meeco Waterboy moisture meter (Warrington, PA) with a range of 1–5000 ppm and an accuracy of ±5%. A Cole Parmer model 00122QA pressure gauge was used for continuous pressure monitoring of gas flow to maintain the pressure of the gas at a desired level of 40 psig. The flow rate of the gas inside the cell was 100 mL/min. The volume of the sample glass cell including the plumbing was 0.5 cm³, thus ensuring fast exchange of gases. Typically 10–20 min will be needed to stabilize the MCL to reach a stable baseline prior to the measurement.

2.3. Deflection and frequency measurement

A MCL was placed in a flow-through glass cell (Veeco Instruments, Santa Barbara, CA) and dry nitrogen gas was passed through the cell at a constant 100 mL/min flow rate during each experiment. When the stable baseline was reached the moisture gas was switched in for testing.

The bending of the MCL was measured by monitoring the position of a laser beam reflected from the gold-coated side of the MCL onto a four-quadrant atomic force microscope (AFM) photodiode. We define bending toward the gold side as “upward bending”; “downward bending” refers to bending toward the Al₂O₃ side. When the adsorption occurs on the Al₂O₃ surface, in general, the upward bending is caused by repulsion or expansion of molecules on the Al₂O₃ surface, which is so called compressive stress.

Frequency tests were made using a reported method that improved the amplitude of cantilever vibration and Q factor value by using a mixed positive signal feedback mechanism [22]. A custom built electronic amplifier was used to amplify the signal detected by the position sensitive photodiode from different quadrants and to compute the vertical displacement. A resonant frequency peak was obtained when the phase of the driving signal and the vertical displacement signal from position sensitive diode matched and measured using a dynamic spectrum analyzer.

3. Results and discussions

Both static and dynamic modes of MCLs were used to compare the sensing performance of MCLs prepared from Method I and Method II for measurement of low-level moisture.

3.1. Deflection of the MCLs

Fig. 2 compares the bending responses of MCLs prepared by Method I and Method II to 200 ppm moisture in nitrogen at a 100 mL/min flow rate. The moisture gas was switched in at the marked time. The MCLs underwent upward bending. After approximately 5 min, the dry nitrogen was switched back through the fluid cell, and the MCL bent downward back to their original positions. The response time to reach equilibrium was approximately 200 s. Fig. 3 shows the MCLs maximum deflection amplitude vs. the moisture concentration. The maximum deflection amplitudes of the MCLs were proportional to the concentrations of moisture. The lowest detectable concentration with Method II was approximately 0.5 ppm, which was improved over the MCLs prepared using Method I with a detection limit at approximately 30 ppm. This sen-
sitivity is as competitive as other mature techniques in the market. The detection limit of moisture is of the 100 ppb to 1 ppm level with electrolytic technique [23] or optical techniques such as FTIR spectroscopy [24] or semiconductors [25]. It is noteworthy that in our previous studies using the method I, the sensitivity we obtained was 10 ppm when relatively thinner Al$_2$O$_3$ film (100 nm in thickness) was used. For direct comparison with the MCLs by Method II, the aluminum film in MCLs from Method I in this study were 500 nm in thickness.

The larger MCL deflection suggests larger surface stress change on the MCL surface with porous Al$_2$O$_3$ coating, which may due to the larger surface area of the porous structure. For a 96 nm maximum deflection corresponding to 200 ppm of moisture, the surface stress change was 0.25 N/m according to Eq. (1). The lifetime tests were conducted on MCLs with 6 months storage under ambient condition. The deflection of these MCLs showed a similar profile and bending amplitude to those in Fig. 2.

The effect of alcohols is a major concern of many moisture meters for low-level moisture detection since the alcohols generally interfere with moisture detection and cause errors. Our previous work showed that the Al$_2$O$_3$-modified MCLs prepared by Method I were not affected by alcohols, which qualifies them for accurate moisture detection without calibration when alcohols exist in the environment. The potential interference of alcohols on the porous Al$_2$O$_3$-modified MCLs was also evaluated in this study. No deflection of porous Al$_2$O$_3$-modified MCLs was observed upon exposure to 200 ppm alcohol. This result is consistent with our previous observations, i.e., the MCL response to moisture was not interfered by alcohols.

3.2. Frequency change of the MCLs

MCL frequency vs. time under different moisture levels was also investigated. The MCLs prepared by the two methods were compared. For each method, five MCLs were tested. The frequency of MCLs prepared from Method I and Method II in dry nitrogen were 28,870 ± 25 and 23,500 ± 50 Hz, respectively. This initially lower frequency of MCLs by Method II might be a result of the lower spring constant of the porous Al$_2$O$_3$ film prepared by Method II. MCLs prepared by the same method had a ±3% difference in their resonance frequencies. The MCLs used in these experiments were triangle silicon MCLs that have a surface area of 1.12 × 10$^{-2}$ mm$^2$.

Fig. 4 shows the frequency of the MCLs vs. time on exposure to 200 ppm moisture. The moisture gas was switched in at the marked time. The response profiles of the two MCLs prepared by the two methods were quite similar. The frequencies of both MCLs decreased quickly on exposure to moisture and returned fully to their initial frequencies when N$_2$ was switched in to replace moisture. Both MCLs showed reproducible response to moisture.

The two MCLs were different in their frequency change percentages and response times. The frequency change of the MCL by Method I was 25 Hz, or 0.886% frequency change, corresponding to 1.85 × 10$^{-11}$ g of water adsorption on the MCL surface according to Eq. (2). The MCL prepared by Method II, however, showed a significant 300 Hz frequency decrease, or 1.27% of frequency change, corresponding to 41.76 × 10$^{-11}$ g of water adsorption on the MCL surface. These results demonstrated the enhanced adsorbing capacity of the porous aluminum oxide film due to its larger surface areas.

The frequency decreases on exposure to moisture reached their equilibrium in 10 and 15 s for MCLs prepared by Method I and Method II, respectively. The frequency recovery took approximately 15 and 30 s for MCLs by Method I and Method II, respectively, when N$_2$ was switched in to replace moisture. These slightly longer response and recovery time of MCLs prepared by Method II was a result of longer adsorption and desorption time related to porous structures of the aluminum oxide film. Although relatively slower, the response of the MCL sensors prepared by Method II has an advantage in response time over other methods such as an electrochemistry method, which took approximately 2 min to reach equilibrium.

A control experiment performed with an Al/Au/Si/Au MCL to moisture showed no change in resonance frequency. Fig. 5 shows the MCLs resonance frequency change vs. the vapor concentration. The frequency changes of the MCLs were proportional to the concentrations of moisture. The frequency decreased as the concentration of moisture increased. The lowest detectable concentration by Method II was approximately 1 ppm, which was more sensitive than those prepared using Method I with a detection limit at approximately 10 ppm.

Lifetime experiments conducted on MCLs stored for 6 months under ambient condition showed a similar frequency change profile to those in Fig. 4.

It is not very clear why it took longer time for the deflection of the MCLs to reach equilibrium than the resonance frequency. One
possible explanation is that the water molecules adsorbed on the MCL surface in the initial stage did not have effective contribution to the MCL bending since the scattered molecules did not interact with others to generate the surface stress. The water molecules adsorbed on the MCLs surface in the later stage, although in a relatively smaller amount, contributed significantly to the surface stress that bent the MCLs. It took longer time for the molecules in the later stage to be adsorbed on the surface due to steric effect.

4. Conclusion

MCLs coated by aluminum oxide prepared by thermal oxidation and anodization process were compared for low levels of moisture measurement. Both the deflection and frequency change showed the MCLs prepared by the anodization process were more sensitive than those by thermal oxidation. Porous aluminum oxide films by the anodization process have a larger surface area and a higher moisture absorption capacity than that of plain aluminum oxide films. Comparing to the current moisture detection systems, the microcantilever sensor has a relatively fast response. Other characteristics including the long-term stability and especially non-interference from alcohol make the cantilever approach very competitive. Our results showed that porous Al2O3-coated MCLs are excellent sensors for low-level moisture detection and may be used for moisture monitoring in low-level moisture environment.

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References


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