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Microcantilever Sensors with Chemically Selective Coatings of Ionic Liquids

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Introduction

In recent years, microcantilevers (MCs) have been explored—for their role as physical transducers in chemical, physical, and biological sensing systems—as part of micro-electro-mechanical systems (MEMS) to detect gas- or liquid-phase species.[1–4] MCs respond to environmental stimuli, such as gaseous contaminants in the atmosphere or dissolved contaminants in liquids. These stimuli affect the micromechanical characteristics of the transducers, which can be monitored using optical, electronic, or other means. The response of MCs is related to changes in their physicochemical properties such as mass, resonance frequency, and energy content. Changes in the intrinsic stress and loaded mass of the MC that result from interfacial processes (i.e., sorption and desorption) lead to direct, highly sensitive, and rapid detection of chemical analytes. As the size of MCs becomes smaller, their mechanical reaction may begin to share similarities with the vibrational mode of molecules.[3,4]

The responses of MCs, which are representative of the micromechanical characteristics of the cantilevers, can be measured in several ways. For example, changes in the loaded mass of cantilevers result from the uptake of chemical species present in the environment. Changes in surface area or mass loading on the MC surface can modulate surface stress because of the thin geometry of MCs, which leads to extremely high surface-to-volume ratios. If the external gravitational, magnetic, and electrostatic forces are negligibly small, the gradient of mechanical stress between the two sides of a cantilever is the only significant factor in cantilever deformation. MC bending resulting from differential stress on its opposite sides can be described by the differential stress Stoney equation: $\Delta z = \frac{1}{2}\frac{l^2}{R} = \frac{3l^2(1-\upsilon)}{Et^2}\Delta\sigma$, where l is the length of the cantilever; υ and E are Poisson's ratio and Young's modulus for the substrate, respectively; t is the thickness of the cantilever; and $\Delta\sigma$ is the differential surface stress.[1]

In this study, the effect of a coating of ionic liquid was investigated as a means to enhance the differential stress on the cantilever. Also, the modulated surface stress can change the resonance frequency of MCs. The resonance frequency of the mechanical resonator can be described by $f_{0,Q} = \frac{1}{2^{3/2}\pi}\sqrt{\frac{k}{m_0}}\frac{\sqrt{2Q-1}}{Q}$, where k is a spring constant of the cantilever; m_0 is an effective suspended mass; and Q is a mechanical quality factor that is inversely proportional to the damping coefficient, defined as $Q = \frac{2\pi W_0}{\Delta W}$. Here, W_0 and ΔW are the accumulated and dissipated mechanical energy per vibration cycle, respectively.[1] A resonance frequency shift resulting from the interaction of MCs with their environment may be caused by several mechanisms, for example: adsorbate-induced mass loading (m_0), chemically induced changes in the cantilever stiffness (k), and mechanical damping by the viscous medium (Q).

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Several published reports confirm that MC-based sensors with a thin solid film (e.g., gold film) are applicable for detection of specific chemicals.[2,5–7] Efforts have also been made to increase the magnitude of the signal, because the surface stress of a smooth cantilever surface is relatively small. Cantilevers with nanostructured surfaces or grooved-surface cantilevers showed enhanced output signals.[6,7] For instance, grooves on cantilevers reduce stress-induced slippage of the film, thus leading to enhanced detection sensitivity of MCs.

This work has demonstrated that liquid-phase coatings can replace solid-phase chemical treatment as chemical sensors for gas-phase analytes. Ionic liquids were chosen as coating materials because they are in liquid state at room temperature and hence are easily applied to the cantilever. Ionic liquids are composed entirely of ions, similar to the ionic melts that can be produced when normal metallic salts are heated.[8–10] Because of their extremely low vapor pressure, ionic liquids constitute a new class of materials that can be used as room-temperature solvents in chemical separations and catalysis applications. Some ionic liquids have characteristics that could prove favorable for use in sensors: for example, air and water stability (i.e., extremely low vapor pressure and solubility), wide liquidus range, and relatively favorable viscosity or density characteristics.[8,10,11] Ionic liquids are good candidates for MC-based sensor coatings when they are characterized with high viscosity to prevent migration of the ionic liquid to the other side of the MC, and low vapor pressure or strong hydrophobicity for a good stability of the coating under exposure to a gas or liquid flow. Depending on the physical phenomenon involved, a coating of ionic liquid can swell or shrink. For example, sorption of analytes by an ionic liquid may cause swelling of the coating; likewise, desorption may cause shrinking. Such characteristics make these ionic liquids suitable for detection of analytes in liquid or atmospheric environments via MEMS.[12] The response mechanism for a MC coated with ionic liquid likely involves an interplay between the surface tension of the liquid and its wetting properties with respect to the MC surface. It is anticipated that both the properties may be affected by changes in the chemical environment and contribute to the MC response. Some ionic liquids also have strong affinities for selected chemical species. Sensors comprising multiple MCs, each with a different ionic liquid coating can not only detect targeted analytes but also help identify chemical speciation. The objective of this work is to investigate the possibility of gas- and liquid-phase detection of analytes with ionic-liquid-coated MC sensors. The ability of the MC sensors to detect analytes is expressed as the change in the resonance frequency or in the response signal proportional to the MC deflection because of the presence of the analyte.

Materials and Methods

Commercially available silicon MCs from MikroMasch (Sunnyvale, CA; US distributor; http://mikromasch.com/) were used in this study. The cantilevers are rectangular in shape with 1.1 ± 0.1 μm thickness. The length and width of the MCs are on the order of 400 and 100 μm, respectively. The ionic liquid used in this work is $P_{666,\ 14}$ LABs (trihexyltetradecylphosphonium dodecylbenzenesulfonate) obtained from Rex Ren (Wesleyan University, CT), which has a sulfonate anion. This is a water-insoluble ionic liquid that has a relatively high viscosity at room temperature,[10,11] stability in water and in the atmosphere, and extremely low vapor pressure. These characteristics make its use in detecting both gaseous and liquid contaminants possible. Both low vapor pressure and high viscosity help preserve the stability of ionic-liquid coatings and consistency of the measurements.

The ionic liquid was deposited on the cantilevers by a micro-spotting or painting technique. From a bulk quantity, an appropriate amount of ionic liquid was transferred onto a cantilever surface simply by touching with a thin, flexible microfiber filament or sharpened stainless steel wire.

MCs used as chemical sensors bend as a result of the difference in surface stresses between the two sides of the asymmetric cantilevers. One side of an asymmetric MC was coated with a thin chemical film of ionic liquid that sorbs target analytes, and the other side was clean. The surface energy of the chemically treated side changed because of the interaction of contaminants with ionic liquid, while the opposite side of the cantilever was passive. The bending of a cantilever and its resonance-frequency shift resulting from sorption or desorption of a target analyte was monitored using a position-sensitive photodetector. A laser beam was focused onto the cantilever tip, and the position of the reflected spot was monitored by the position-sensitive photodetector (see Figure 1). Resonance frequency and cantilever deflection, among other MC responses to vapors of volatile chemicals, were investigated.

Analytes were introduced via a syringe into a flow cell where the cantilever was located. Acetone, ethanol, or water vapors were produced from injection of the pure liquid-phase chemicals in the syringe. All analytes were introduced into the cell with nitrogen gas flow. Nitrogen is the most abundant gas in the atmospheric environment; thus, detection of nitrogen-based analytes was used to simulate the detection of actual contaminants in the atmosphere.

The shape and amount of the ionic liquid coatings were slightly different for each cantilever. Therefore, to minimize these differences, cantilever painting was standardized at the same location and height for each surface. Two approaches were used to optimize the uniformity of the ionic-liquid coating on the MC surface and, consequently, the magnitude of the detection output. The first was based on mixing a nanosized powder with an ionic liquid to achieve a uniformly distributed thin coating. In this method, aluminum oxide nanopowder (40–50 nm average size), obtained from Sigma-Aldrich (St. Louis, MO), was mixed with ionic liquid prior to applying the coating. The aluminum oxide was not expected to react with the analytes in this study and it was also assumed that no chemical reaction occurred between the particles and ionic liquid, as the ionic liquids have been shown to be inert to other salt compounds.[10] The particles helped to increase the viscosity of the ionic liquid, which was useful in producing a thin, flat, stable ionic-liquid film. A thinner coating provides a higher ratio of surface area to volume; thus, the mixing method overcame the relatively small surface stress of the smooth cantilever. The second approach to improve the detection level was the use of nano-

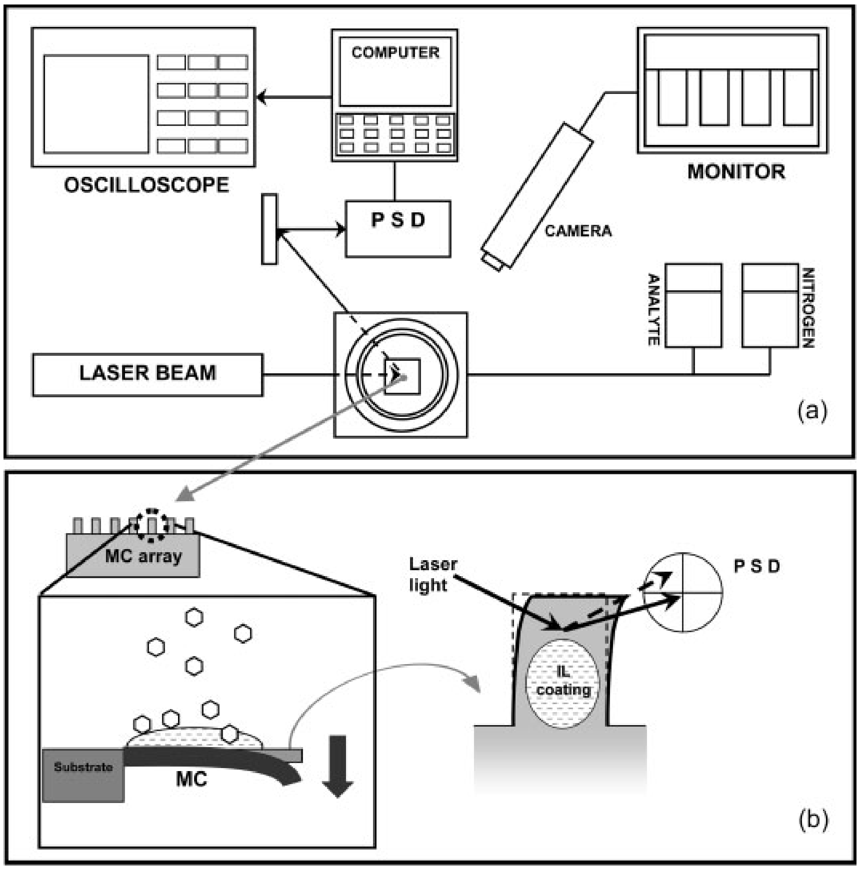

Figure 1. (a) Schematic representation of the analyte delivery system, consisting of an analyte-containing syringe and a nitrogen gas tank; (b) illustration of MC deflection due to analyte sorption or desorption by the ionic liquid (IL) coating.

A laser beam is focused on the cantilever tip, and the position movement of the reflected spot is monitored via a position-sensitive detector (PSD). The PSD is connected to an oscilloscope for direct observation of the signal and to a computer for data acquisition.

structured cantilevers prepared by a focused ion beam (FIB). To increase the surface area of contact with the ionic-liquid coating, FIB was used to make grooves of controlled depth on the cantilevers. Because the cantilever surface with increased contact area holds ionic liquid more effectively, the coated ionic liquid on the grooves was expected to increase the sensitivity for detection of analytes.

Results and Discussion

Detection of gaseous analytes via deflection of MCs

Ionic-liquid-coated MCs were first used to detect water vapor, acetone vapor, and ethanol vapor in nitrogen gas flow. The responses from three different cantilevers (C1, C2, and C3) were recorded for a period of 100 s each. Cantilevers C1, C2, and C3 were coated with the same ionic liquid by the standardized painting procedure to minimize the differences in shape and amount of the coatings. Therefore, the cantilevers were expected to have similar features in their response curves. The results in Figure 2 show the distinctive features of the responses. Measurements of the deflection of MCs show that the chemical with highest volatility had the largest response. At the beginning of the response, output signals show an initial peak. Although the initial peak is relatively small for the water vapor output, all the signals show initial peaks that later relax to a steady-state value. This initial peak seems to be a unique feature for the response from ionic-liquid-coated MC sensors; in previous studies, MC-based sensors with solid-film coatings showed a response following simple monotonic kinetics without an initial peak.[7]

Ionic liquids are generally regarded as stable chemicals with extremely low vapor pressure at room conditions. However, compared with solid-phase coatings, liquid coatings may be less stable over time or when subjected to external stimuli. To ensure the stability or reproducibility of response measurements, the same response of ethanol in nitrogen was measured after a period of several days. The results (not shown) confirmed that no significant change in the response of the ionic-liquid-coated cantilevers occurred over a relatively long period of time.

MC surface modifications

It was assumed that the mixture of aluminum oxide powder and ionic liquid would better wet the cantilever surface. However, the mixture did not spread evenly on the cantilever surface; therefore, a 10% dilution of ionic liquid with 2-propanol was used to form a smooth coating. Three varying

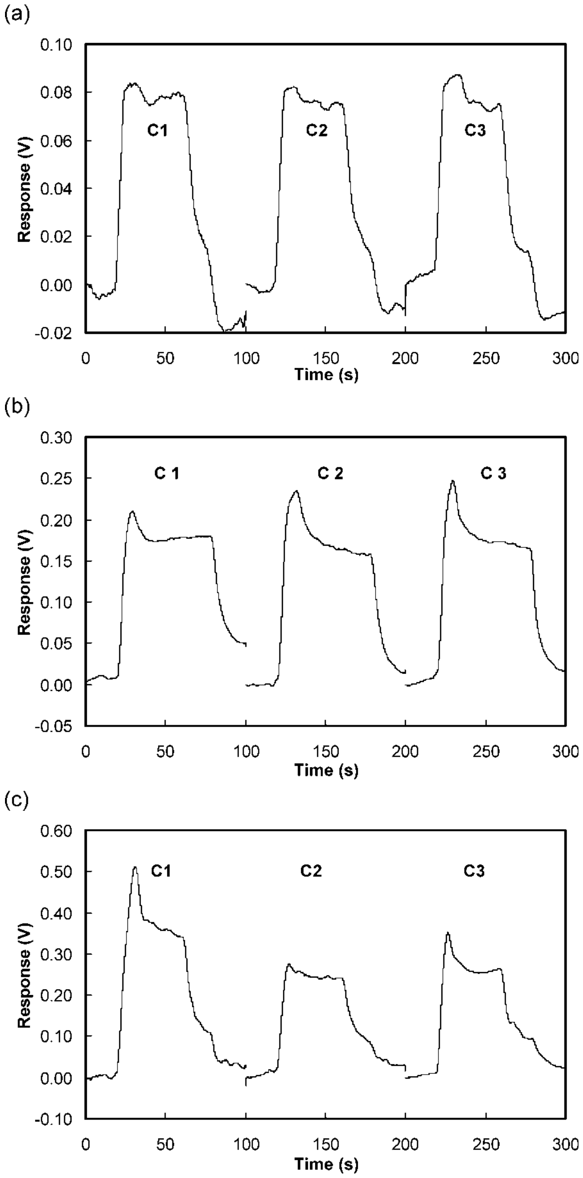

Figure 2. Responses to (a) water vapor, (b) acetone vapor, and (c) ethanol vapor from three different cantilevers with the same ionic liquid coating.

To maximize the response, it is preferable that the ionic liquid be located at the edge (away from the free end) of the cantilevers.

combinations of diluted ionic liquid and particle-mixed ionic liquid were used (Figure 3a). One cantilever (C6) was covered with particle-mixed ionic liquid, a second (C7) was coated with particle-mixed 2-propanol and water, and a third (C8) was clean. All three cantilevers (C6, C7, and C8) were then covered with 10% diluted ionic liquid in 2-propanol. As a reference, the other cantilever (C9) remained blank (Figure 3b). Even though the higher surface area cantilevers (C6 and C7) led to a greater response with ethanol vapor, as shown in Figure 3c, the response level was not much higher than that achieved via the MC (shown in Figure 2) that had been coated with undiluted ionic liquid without particles. The signal from the blank MC showed noise level fluctuation.

In the second approach to achieve a uniform, thin coating of ionic liquid on the cantilever surface, a nanostructure was applied to the surface of MCs using FIB milling. As shown in Figure 4a, the ionic liquid was spread evenly on the structured MC surface. As the number of the cantilever in the sequence increased, the grooves were made deeper (i.e., cantilever C2 had the shallowest grooves and cantilever C5 had the deepest).

Cantilevers C3 and C5 were tested in terms of response to water and ethanol and showed very different responses. Figures 4c, d show the response of cantilevers C3 and C5, respectively. Although a similar positive response to ethanol was detected for the two MCs, the responses to water showed opposite signals. This indicates that one response resulted from swelling—and the other from shrinking—of the coated ionic liquid. The only difference between the two cantilevers was the depth of the grooves; those of C5 being deeper than those of C3. Despite the similar applications of the coatings of ionic liquid, this response indicates that the difference in groove depth can lead to different behavior

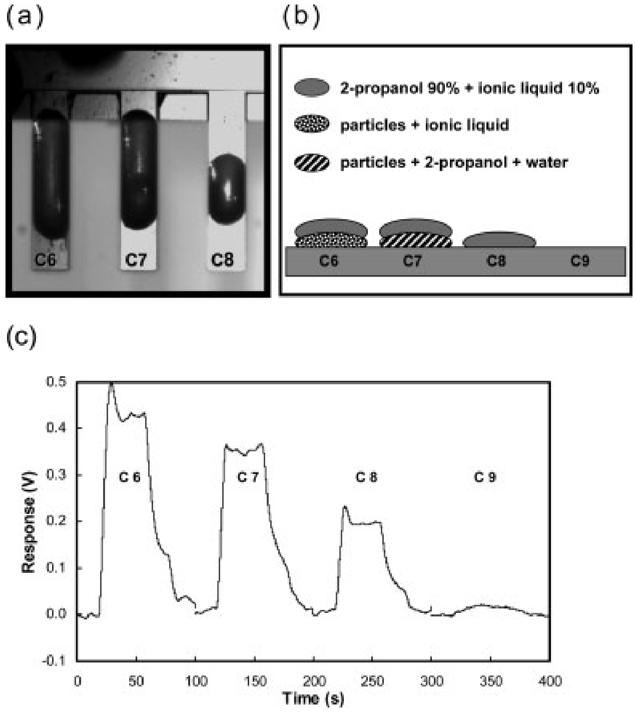

Figure 3. (a) Micrograph showing results of different coating applications; (b) specific mixtures used for coating: cantilever C6, mixture of aluminum oxide particles with ionic liquid (covered with 10% dilution of ionic liquid in 2-propanol); cantilever C7, mixture of aluminum oxide particles with 2-propanol and water (covered with dilution of ionic liquid in 2-propanol); cantilever C8, covered with 10% diluted ionic liquid in 2-propanol droplet (without particles); cantilever C9, blank; (c) response of all cantilevers to ethanol vapor.

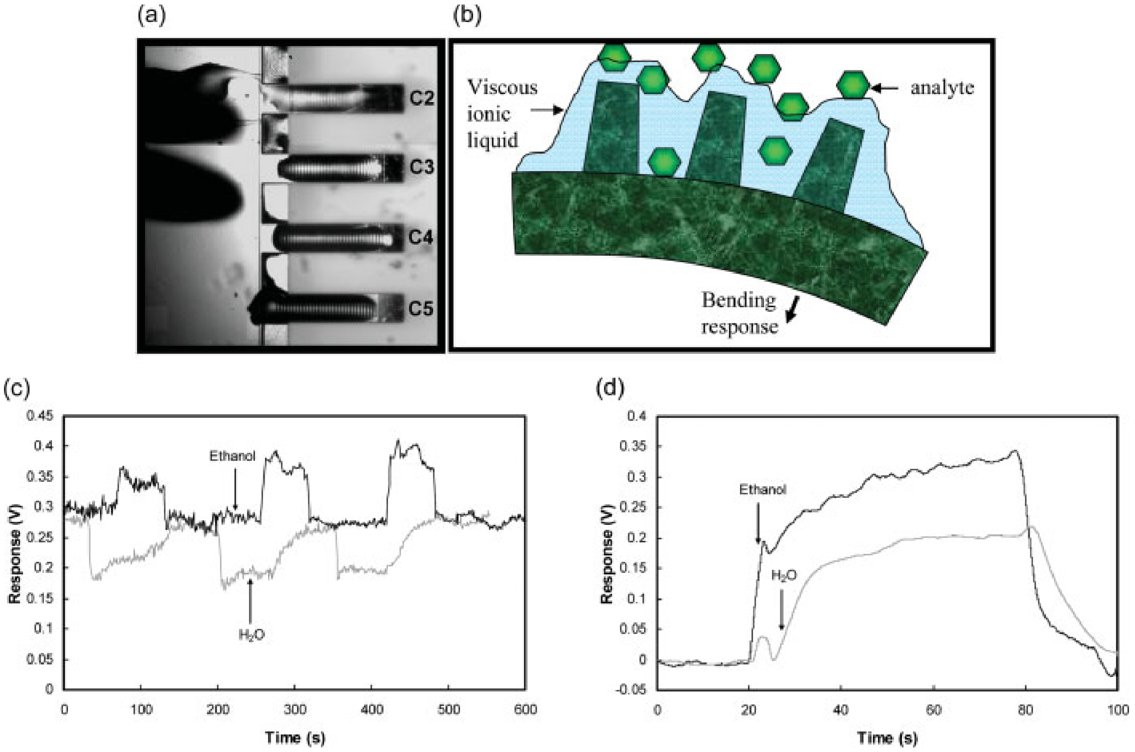

Figure 4. (a) Micrograph showing ionic liquid coating on structured MCs; (b) schematic of MC bending; (c) response of cantilever C3 [note that these are two different experiments and that the analyte (ethanol or water) is not introduced at the same time schedule]; (d) response of cantilever C5 to water vapor and ethanol vapor.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(i.e., swelling versus shrinking) of the coatings and thus different responses to analytes.

Detection of characteristic atmospheric pollutants

The response to CO_2 was detected with a grooved cantilever (C3 in Figure 5) for a period of 100 s, similar to previous experiments. The response in Figure 5 differs from those to the other analytes, showing a unique feature that is indicative of the affinity between the ionic liquid and the analyte. As with other analytes, a peak occurs at the first part of the injection. However, the response decreases continuously and slowly even after the inflow valve of the analyte is shut down. Such a response indicates a high affinity between the ionic liquid and the analyte (CO_2), leading to a slow desorption after the CO_2 flow is turned off.

Resonance frequency shift

A resonance frequency shift, another feature that can be detected from coated MCs, was detected for both cantilevers C3 and C5 as shown in Figure 6. The detected resonance frequency shift varies with the type of contaminant. In Figures 6a, b, the frequency shift for cantilever C3 to NO_x was greater than that for cantilever C5 to ethanol. Furthermore, the results for both cantilevers are greater than those for a blank cantilever (results not shown). Comparing the frequency shift observed in this study for ionic-liquid coated MCs with the frequency shift observed by Baltus et al.[13] for an ionic-liquid coated quartz crystal microbalance, the frequency shift for MCs is on the order of hundreds of Hertz while that of the quartz crystal microbalance is only a few Hertz. This behavior is due to the small mass of the MCs, as compared to that of the quartz crystal microbalance. Thus, the results of this study demonstrate that changes in amplitude as well as oscillation frequency shift can be measured and correlated for contaminant detection.

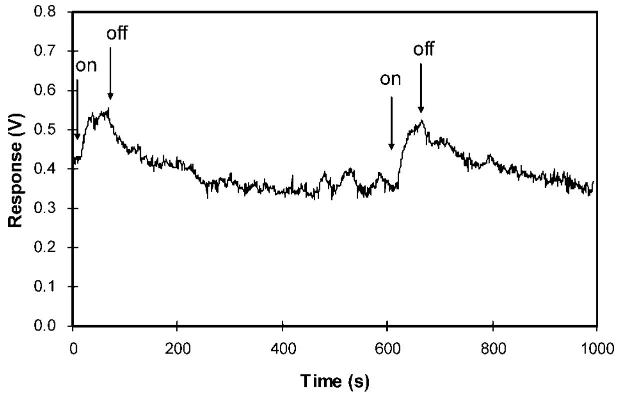

Figure 5. Response of cantilever C3 to CO_2.

The slow response after the inflow switch was turned off is a unique characteristic of the CO_2 signal.

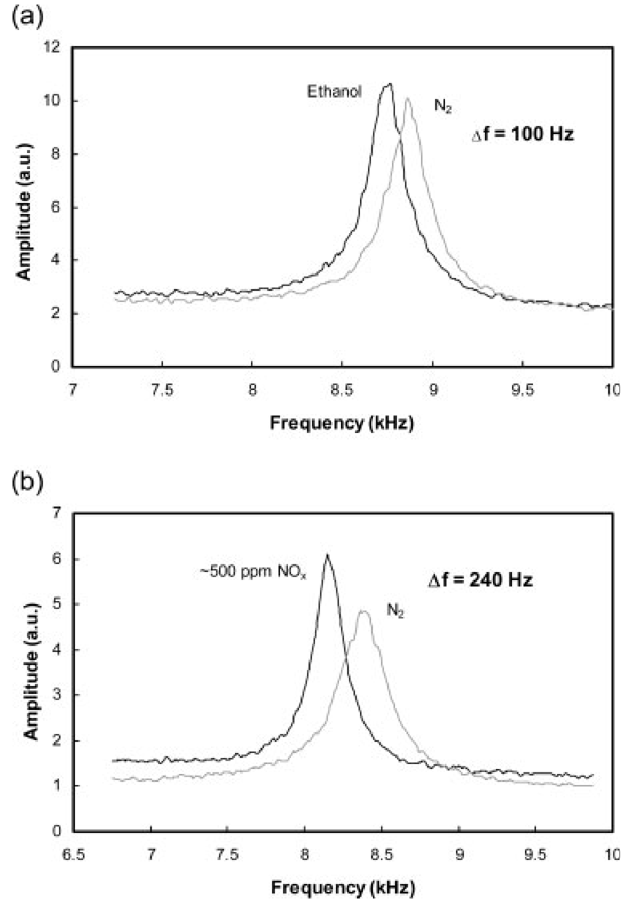

Figure 6. Resonance frequency shift of (a) cantilever C5 and (b) cantilever C3.

Conclusions

In summary, ionic-liquid-coated MCs showed significant responses to water, acetone, and ethanol vapor. The coating in this system was stable, and the response was reproducible for several days. A coating made from a mixture of aluminum oxide particles in a 10% concentration of ionic liquid in 2-propanol was found to be evenly distributed on the MC surface and increased the magnitude of the response. The results for coated ionic liquid on grooved cantilevers differed according to groove depth. In general, ionic liquids proved to be good candidates for MC coatings in sensor applications. Future studies should focus on selective detection of specific chemical species in mixtures of analytes.

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