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Stress-based vapor sensing using resonant microbridges

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We demonstrate that silicon-polymer composite microbridges provide a robust means of water vapor detection at ambient pressure. Volumetric changes in the reactive polymer alter the tension in a doubly clamped structure leading to large and rapid changes in the resonance frequency. We demonstrate stress-based sensing of water vapor in ambient pressure nitrogen using doubly clamped buckled beams coated with a hygroscopic polymer. We show stress sensitivity of around 20 kPa (~170 ppb of water vapor) and subsecond response time for coated microbridges. © *2010 American Institute of Physics*. [doi:10.1063/1.3393999]

A need exists for fast and inexpensive trace vapor detectors. Microsensors based on electrochemical, surface acoustic wave, optical, and mechanical transduction are under investigation to meet this demand.[1] Sensors based on microelectromechanical systems (MEMS) are candidates for a wide range of sensing applications including environmental monitoring;[2] bio- and health analysis;[3–6] and detection of explosives for security use and landmine sweeping.[7–10]

Microcantilevers have been the primary MEMS structures used in sensors research. In these studies, changes in the resonance frequency of the cantilever due to the added mass of analyte or changes in materials properties due to chemical interaction between the analyte and a reactive coating are measured. Inertial mass sensors have proven extremely sensitive in vacuum.[11–13] Various surface coatings and treatments have been developed for use at ambient pressure where sensitivity is lower due to viscous losses.[9,14–16] Alternately, cantilevers are coated on a single side with a reactive layer that swells or contracts upon contact with an analyte and a static deflection is measured.[17] In functionalized cantilever studies, deflection of the composite structure relieves the stress induced by these volumetric changes.

In contrast to these mechanisms, in this paper we demonstrate that the stress from the swelling of a reactive coating can be quantifiably measured by tracking shifts in the resonance frequency of a microbridge. Microbridges ($25\times 6 \times 0.12$ μm) are fabricated from compressively-stressed polycrystalline silicon films which are grown by low pressure chemical vapor deposition over a sacrificial oxide layer. Upon wet-etch release of a doubly clamped bridge the residual stress is relieved by buckling of the structure (toward the substrate in the case of our experiment); see Fig. 1(a), inset. The resonant behavior of these buckled beams has been described by Nayfeh and Emam *et al.*[18,19] We deposit 100 nm of a porous hygroscopic polymer, tert-butylcalix[6]arene (TBC6A), by thermal evaporation onto the bridge. This material has been considered for detection of trinitrotoluene vapors[9] but is shown here to be strongly affected by moisture. Porous polymers commonly swell in proportion to the relative humidity,[20] and the frequency of tensile-stressed doubly clamped all-polymer beams has been shown to decrease with hygrometric expansion and the associated reduction in the included tension.[21]

Swelling of the polymer layer in a composite buckled beam configuration (where the buckling occurs as a response to compressive stress), however, produces an axial load that *increases* the resonance frequency of the fundamental mode. The frequency response of a coated microbridge to water vapor is shown in Fig. 1(a). These shifts are counter to the

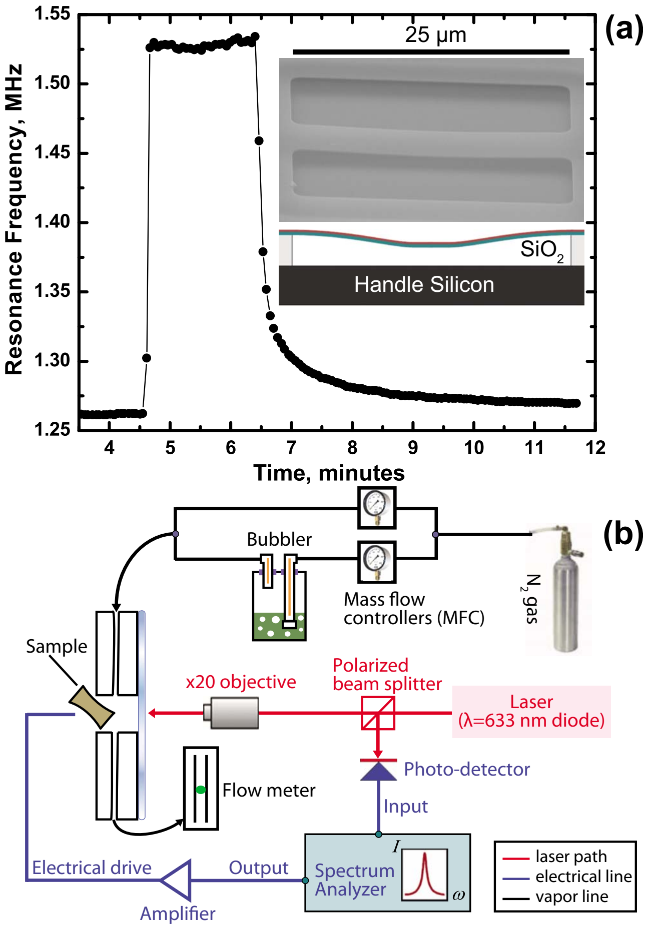

FIG. 1. (Color online) (a) Fast rise in natural frequency (<1 s) of a buckled polycrystalline silicon microbridge resonator coated in a hygroscopic polymer in response to an increase in relative humidity in nitrogen from dry to around 50%. The frequency increases with volumetric expansion of the polymer coating due to the buckled nature of the bridge. Data points are acquired at three-second intervals and the desaturation curve originates from systematic drying of the vapor lines. Inset: SEM and schematic of buckled microbridge. (b) Schematic of the experimental setup including electrical drive, optical detection, and vapor delivery systems.

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effect of added mass, Δm, which reduces the natural frequency as $\Delta f = -(1/2)f(\Delta m/m_{\text{eff}})$, where f is the frequency and m_{eff} is the effective mass of the resonator. We estimate that such mass loading decreases the resonance frequency by less than 15 kHz, which is small compared to the frequency increase observed, and we neglect the added water mass in further calculations assuming the stress-induced frequency rise overwhelms any inertial mass-based frequency reduction.

Applying the equivalent beam method of Timoshenko[22] to our composite beams we find that the flexural rigidity (EI, where E is the Young's modulus; I is the moment of inertia, $I = (1/12)wt^3$; w is the width and t is the thickness) is changed by roughly 2% due to the addition of the polymer. Thus in this configuration the main role of the polymer is to alter stress, since the polymer does not significantly affect the flexural rigidity of the composite structure.

The experimental setup is depicted in Fig. 1(b). In this experiment, MEMS are electrostatically driven and their motion is detected optically using an interferometric technique[23] through the window of a flow cell. The resonance spectrum of the microbridges is monitored in real-time as the relative humidity of the nitrogen is varied between zero and nearly 100%. The relative humidity is controlled using a pair of mass flow controllers that vary the mixing ratios of dry nitrogen and nitrogen aerated through a column of deionized water. Although no humidity standard was used in this experiment, we assume the aerated nitrogen to be fully saturated.

Devices are placed in a flow cell of volume 0.7 cm^3 under continuous flow conditions of 20 SCCM. We observe that the characteristic time for the device to stabilize at a new frequency, or its rise time, changes in accordance with the flow cell time constant, $\tau = \text{cell volume}/\text{flow rate}$, for varied gas flow rates, which do not otherwise affect device performance. From this we determine that the rise time is set in this experiment by the time required to replace the gas in the flow cell volume. Thus the characteristic resonator response time is shown to be below one second. The longer time constant for the desaturation curve in Fig. 1(a) is believed to result from the time associated with the systematic drying of the flow lines, although we cannot rule out slower water desorption kinetics.

Development of beam theory has a long mathematical history[24] but only recently have theorists developed an exact analytical solution to the resonant behavior of buckled beams.[19] If the nonlinear, damping and forcing terms are dropped from the differential equation of motion, the resonant frequency relationship to the axial (compressive) load of a buckled beam may be obtained in closed form. For the fundamental mode of the first buckled configuration, f_0, in which our devices operate

$$f_0 = \sqrt{\frac{2}{m_l l^2}\left(S - 4\pi^2 \frac{EI}{l^2}\right)}. \tag{1}$$

Here, m_l is the per-length mass, l is the undeformed length of the beam, and S is the axial load on the doubly clamped beam.

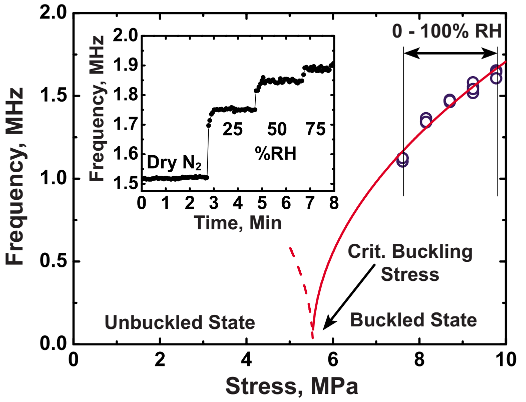

FIG. 2. (Color online) Changes in resonance frequency of a buckled beam. A hygrometric polymer coating expands in proportion to relative humidity (RH). Extrapolation of the fit to the data illustrates potential for high sensitivity near the critical buckling stress. Inset: Resonance frequency shift of a coated microbridge in response to stepped changes in relative humidity. Variation in frequency among the devices presented arises from varied timing in the release step.

Ignoring the added water mass and changes in the Young's modulus of the polymer, the stress in the buckled beam may be calculated directly from the resonant frequency measurements, Fig. 2, inset. The second term under the radical in Eq. (1) describes the critical load at which the beam buckles and the resonance frequency drops to zero. In our devices this load corresponds to an axial (compressive) stress of 5.5 MPa, depicted in the fit of the data in Fig. 2. The inbuilt stress, ~7.6 MPa exceeds the buckling stress and results in the static bowing of the beam. Swelling of the polymer when exposed to nitrogen over the full humidity range produces an additional axial stress of around 2.2 MPa. The linearity of the hygrometric expansion of the polymer is generalized to TBC6A from Buchhold *et al.*[20] and yields the hygrometric strain $\varepsilon_{\text{hyg}} = \alpha_{\text{hyg}} RH$, where α_{hyg} is the linear coefficient of hygrometric expansion and RH stands for the relative humidity, which varies between zero and one. The stress imparted by polymer swelling is thus

$$\sigma_{\text{hyg}} = \Delta\sigma = E_{Si}\alpha_{\text{hyg}} RH. \tag{2}$$

From Eq. (2) and the measured change in frequency of a microbridge with RH we calculate the coefficient of humidity-induced volume expansion to be $\alpha_{\text{hyg}} = 18$ ppm. We find that the frequency stability of the resonators limits our resolution to 3 kHz in the limit of low humidity; see baseline of Fig. 1(a). In our experiment, 3 kHz resolution corresponds to a minimum detectable change in stress of ~20 kPa, or 170 ppb of water vapor.

Sensors operated near the critical stress of buckling could show greatly increased stress sensitivity since the frequency-stress curve becomes steep as the stress approaches the critical stress. The maximum stress sensitivity obtainable is likely to be set by geometrical imperfections in the beam,[25,26] which in effect smooth the transition from the unbuckled to the buckled state. The stress sensitivity of a microbridge varies strongly with the silicon layer thickness, and thus in detector applications these structures benefit from the thin films available in MEMS processing. When optimized, thin microbridges operating near the critical buckling stress could provide a very high sensitivity platform for sensing.

Improved resolution of frequency for operation in gas is possible through improvement of the quality factor, Q, by optimization of the device geometry. Measurements of bare and coated microbridges in vacuum yield nominal Q of 4000 and 400, respectively, compared to a quality factor of at most

10 in air ($Q=3$ for 6 μm wide beams; $Q=10$ for 2 μm wide beams). This suggests that acoustic dissipation (viscous damping) rather than intrinsic materials loss is the primary energy dissipation mechanism at atmospheric pressure.[27] The quality factor of 400 for the composite structure implicates intrinsic losses in the polymer as the predominant dissipation mechanism in vacuum.[28] Air damping in resonant MEMS remains an active area of research.[29,30] Studies of resonant operation of MEMS at atmospheric pressure suggest a path toward decreased dissipation ($1/Q$) by taking advantage of higher frequencies to decrease acoustic coupling to air.[27,31]

Microbridges enable direct transduction of stress variation into the frequency or phase domain, which is advantageous for its high measurement accuracy and for integration of sensors into radio frequency circuitry. Structures created from doped silicon, such as ours, are compatible with the electrical detection techniques introduced by Truitt *et al.*,[32] as well as amenable to readout via embedded piezoelectric elements.[33] Because of their different responses to stress, operation of microbridges in conjunction with cantilevers or other variously coated, sensitive structures could contribute an orthogonal response to assist in unique identification of analytes in electronic nose applications.

We have shown that resonant microbridges coated with TBC6A can be sensitive to relative humidity. While this material has been shown to be sensitive to other volatile compounds, those wishing to employ hygroscopic materials for detection must control carefully for moisture. Common mode canceling can be employed to account for environmental factors such as atmospheric pressure or temperature variations.

Stress-based resonant sensing using microbridges represents an unexploited method for detection of vapors applicable to electronic noses operating in ambient conditions. Surface coatings under development for deflection-based cantilever sensors can be applied to doubly clamped structures where the fast response and readout in the frequency domain commend them to sensor applications. Doped polycrystalline silicon resonators such as those described in this work are compatible with electrical detection and integration into industrial complementary metal-oxide-semicounductor (CMOS) processes,[34,35] where stressed polycrystalline silicon layers are common. Fabricated through simple top-down processing, microbridge sensors represent an excellent example of advantageous scaling in MEMS. Resonant detection of vapor through the mechanism of stress has potential to improve real-time atmospheric gas sensing technology.

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