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Stress-based resonant volatile gas microsensor operated near the critically buckled state

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We describe sensing of chemical vapors from the atmosphere using critically buckled polycrystalline silicon doubly clamped mechanical resonators coated on one side with polymethyl methacrylate (PMMA). Our method of sensing is based on stress-induced resonance frequency shifts through volumetric swelling of the 60 nm thick PMMA layer resulting in altered tension in the beams. The stress change produces shifts in the resonance frequency as large as 150% of the baseline frequency. In order to maximize the sensitivity, we tailor residual stress of the polycrystalline silicon resonators to slightly exceed the critical buckling stress. We incorporate a relatively large gap between the bridge and a substrate to provide optical readout and minimize squeezed film effects. We show that the larger gap results in substantial improvements of the quality factor and frequency stability of our resonators under ambient pressure and temperature conditions compared to previous implementations. These lead to resonance frequency shift per concentration change of ethanol vapors of \sim 360 Hz/ppm with a response time of a few seconds measured in our gas delivery and readout system. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4720473]

I. INTRODUCTION

There is a demand for fast, sensitive, and inexpensive gas sensors. Aiming towards large-scale lab-on-a-chip integration, the development of microsensors implemented by micro and nanoelectromechanical systems (MEMS/NEMS) (Refs. 1 and 2) are in progress to be used for various biological, chemical, and environmental sensing applications.^{3–6} For example, in biomedical and clinical studies, miniaturized olfactory microsensors have shown potential to diagnose diseases such as asthma and diabetes through exhaled breath analysis.⁷⁻⁹ Miniaturized chemical gas sensors have been developed to detect very small amounts of flammable gases and trace explosive gases for public safety and security uses.^{10–13} In these applications, various types of chemical microsensors have been investigated, such as deflection-based functionalized MEMS cantilever arrays,^{14,15} chemiresistors,¹⁶ capacitive chemical microsensors,¹⁷ nanowire arrays,^{13,18} quartz crystal microbalance (QCM),¹⁹ surface acoustic wave (SAW) devices,^{20,21} and mass-based detection in NEMS arrays.^{22,23}

In previous work, we demonstrated the stress-based detection approach and water vapor detection in siliconpolymer composite resonant microbridges (RMBs).²⁴ Doubly clamped RMBs functionalized with thermally evaporated nanoporous polymer film exhibited significant positive resonance frequency shifts in a silicon-polymer bilayer due to stress changes from adsorbed vapors that cause the polymer layer to swell. This mechanism is dominant over massloading effects from the vapors that would induce negative frequency shifts. The RMBs under compressive stress have calculated sensitivity as low as 170 parts-per-million (ppm) with a few seconds response time.²⁴

Here we report the resonance response of polymer-spin coated doubly clamped beams to ethanol, benzene, and water vapor. Our beams operate near their critical bucking stress²⁵ (also known as the Euler stress), where the sensitivity of the devices can be potentially greater than cantilevers or doubly clamped beams far away from the critical stress. This critical stress, σ_{crit} , is known to be²⁵

$$\sigma_{crit} = \frac{\pi^2 E t^2}{3 L^2},\tag{1}$$

where *E* is the Young's modulus, *t* is the thickness, and *L* is the effective beam length. Here we demonstrate functionalization of reproducible spin coated polymer layer of a few tens of nanometers thickness on top of 140 nm thick nearcritically buckled microbridge resonators, yielding sensitivity and response time comparable to state-of-art devices.^{14–23} Table I summarizes estimated sensitivities and response times of some of these methods.

II. EXPERIMENTAL

The RMBs are fabricated using n+ doped polycrystalline silicon (poly-Si) films grown by low pressure chemical vapor deposition (LPCVD) at 596 °C on top of a thermal sacrificial oxide layer. The deposition temperature controls the residual stress in the poly-Si layer and is selected to consistently yield

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Methods	Estimated response time	Estimated minimum detectable concentration	Pressure and temperature	Analyte	
Deflection-based			Atmosphere,	Water, ethanol,	
MEMS array ¹⁴	$\sim 50 \mathrm{s}$	1000–2000 ppm	room temperature	acetone, etc.	
			Atmosphere,	Methanol, water,	
Chemiresistor ¹⁶	$\sim 10 \text{ ms}$	4–5 ppm	room temperature	benzene, etc.	
Nanowire array ¹⁸	$\sim \! 10 \mathrm{s}$	0.1–1 ppm	Atmosphere, 300 °C	Ethanol	
Mass-based detection in				Toluene,	
MEMS array ²²	40 ms	0.6 ppb	Atmosphere, 40 °C	octane, etc.	

TABLE I. Estimated response time and minimum detectable concentration among selected methods for micro- and nano-gas sensors.

near-critically buckled 20 μ m long and 140 nm thick resonators. The thickness of the poly-Si film is approximately 140 nm, while that of the sacrificial oxide is $1.2 \,\mu$ m; both are deposited on a (100) silicon substrate. Doubly clamped beams that are 20 μ m long and 2 μ m wide are patterned, followed by wet-etch release and critical point drying of the suspended beams. The residual compressive film stress is relieved upon the wet-etch release of the beams, which cause the RMBs to be slightly buckled either out of plane or towards the silicon backplane. Prior to their surface functionalization, we deposit a 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (FOTS) monolayer on top of the doubly clamped RMB and substrate surface by molecular vapor deposition. This FOTS monolayer film, which makes the resonator surface substantially hydrophobic, prevents stiction of the bridges to the substrate during the last spin coating process of the functionalizing polymer. A brief low-power oxygen plasma etch removes the FOTS coating from the top surface of the wafer. Approximately 60 nm of polymethyl methacrylate (PMMA), a polymer known as effective for sensing flammable vapors,²⁶ is then deposited by spin coating. The thickness of our PMMA layer is estimated by spin coating a separate silicon piece under the same spin conditions (measured by FilMetrics F40 (San Diego, CA)). A schematic of our fabrication process is illustrated in Figure 1. Both optical microscope and scanning electron microscope (SEM) images of the spin coated RMBs, which are presented in Figures 2(a)-2(c), show that the bridges are buckled and that the spin coated PMMA adhered to the top of the bridges. We find that the midpoint displacements of the non-coated and PMMA-coated RMBs are 137 and 265 nm toward the substrate ($\sim 1\%$ of the beam length) as measured by an optical surface profiler (Zygo, Middlefield, CT). (Thus, the RMBs are near their critically buckled state.) In case that the deposition temperature of poly-Si films during the LPCVD process is considerably higher than the selected temperature (~ 596 °C), we find that the amount of compressive stress exerted in its axial direction notably exceeds the Euler stress given by Eq. (1), which causes the RMB to be highly buckled.²⁷

Before their functionalization, the RMBs are wire bonded and mounted on a dual-in-line package (DIP), after which they are loaded into a flow chamber for device characterization (see Fig. 2(d)). The experimental setup for gas delivery and resonance measurements is described in Southworth et al., where gas concentrations are mixed through a dual channel flow-line.²⁴ The doubly clamped beams are electrostatically driven through a built-in tracking generator of a spectrum analyzer (Agilent Technologies, Santa Clara, CA), which is coupled with DC biasing voltage, and their out of plane motion is detected using an interferometric optical technique.²⁸ In order to maximize the optical reflectance signal, the gap between the poly-Si bridge and the substrate is chosen to be $1.2 \,\mu\text{m}$. The resonance spectrum of the bridges is monitored, as mixtures of dry nitrogen and vapor of interest with various concentrations, are delivered to the devices through the flow line system. Concentrations are



FIG. 1. (a) Fabrication process flow of a critically buckled micromechanical resonator functionalized with PMMA spin coating. Buckling of the bridges is not depicted in this figure.



FIG. 2. (a) Optical microscope, (b) SEM image, and (c) surface profile of the micromechanical bridge after its functionalization, respectively $(20 \,\mu\text{m} \times 2 \,\mu\text{m} \times 0.14 \,\mu\text{m})$. (d) Wire-bonded device chip mounted on a dual in-line package (DIP).

controlled by mass flow controllers in each of two flow channels. The desired concentration of analyte vapor is obtained by altering the ratios of dry nitrogen and analyte vapor through the liquid state analytes. Here we assume that vapors from the analyte channels are fully saturated. Under this assumption and through knowledge of the mixing ratio, we obtain the analyte concentration in parts-per-thousand (ppt) in the high concentration range and parts-per-million (ppm) in the low concentration range. Before each set of measurements, saturated ethanol vapor is loaded into the flow chamber and then fully vented after a few minutes in order to effectively purge the flow chamber, resetting the RMB near the critically buckled and dry state.

III. RESULTS AND DISCUSSION

A. Resonance characteristics

According to the derivation in Appendix, the fundamental frequency of microbridges in the first buckled configuration f_0 can be approximated by

$$f_0 = 2\pi \sqrt{\frac{2EI}{3m_l L^4} \left(\frac{\sigma}{\sigma_E} - 1\right)},\tag{2}$$

where σ is the axial compressive stress and $\sigma_E = 4\pi^2 Er^2/L^2$ is the Euler's buckling stress. Here m_l is the mass per unit length, *I* is the area moment of inertia, and *r* is the gyration radius of the cross-section of the beam. Resonance frequency shift Δf_0 resulting from small effective mass and axial stress variations only (Δm and $\Delta \sigma$, respectively) without other stiffness property variations, can be approximated to the first order by the expression

$$\frac{\Delta f_0}{f_0} = \frac{1}{2} \left(-\frac{\Delta m}{m_{eff}} + \frac{\Delta \sigma}{\sigma - \sigma_{crit}} \right). \tag{3}$$

According to Eq. (3), the resonance frequency may drop due to loaded analyte mass ($\Delta m > 0$) or *increase* due to altered axial stress exerted to the functionalized RMB ($\Delta \sigma$). For a buckled RMB, swelling of the polymer layer alters the stress of the bridges towards more compressive as it reacts with the analyte, causing a positive $\Delta \sigma$ and a rise in the resonance frequency. (On the other hand, the frequency decreases in a pre-buckled RMB configuration when compressive stress is applied as it induces negative change in $\Delta \sigma$.) As the RMB approaches closer to its critical buckling state, the difference between the axial and Euler stress becomes much smaller, which results in relatively higher induced change in normalized axial stress, or $\Delta\sigma/(\sigma-\sigma_{crit})$. (Note that an additional increase in the sensitivity can be expected due to the influence of the stress gradient between the polymer layer and the beam.) In case of a flat beam structure, however, the change in the normalized axial stress is much smaller than that of a critically buckled RMB. The functionalized RMB has fundamental mode resonance frequencies of 1.3, 2.7, 2.9, and 3.6 MHz in dry nitrogen, saturated water vapor, saturated benzene vapor, and saturated ethanol vapor, respectively



FIG. 3. (a) The resonance peaks and qualify factors of a resonant micromechanical bridge surrounded by saturated analyte vapor before baseline subtraction (b) Resonance frequency shift evolution in time of the functionalized micromechanical resonator after exposure to individual saturated analytes following baseline subtraction. In order to extract the response time constant τ , we define as the time taken to achieve 63% (or 1 - 1/e) of the total frequency shift. In case of ethanol vapor, whose concentration is greater than 2.9 parts-perthousand, resonance frequency overshoot effect has been observed. (c) The quality factor vs resonance frequency of the RMB ($\Delta Q/\Delta f = 8.64 \text{ MHz}^{-1}$).

(see Fig. 3(a)), demonstrating large frequency changes due to the introduction of each analyte. These values are obtained without significant deterioration of the functionalized

surface, allowing numerous cycles of consistent device operation with the analytes chosen for this study.

Figure 3(b) shows time traces of the functionalized micromechanical resonator response for each saturated analyte vapor. In this figure, we demonstrate, for saturated ethanol vapor, an approximately 2 MHz increase in the resonance frequency (that is, $\sim 150\%$ of the baseline frequency with dry nitrogen), while less than 0.5% increase in its normalized resonance frequency has been observed for the nonspin coated RMB that has only the FOTS layer deposited on it. In addition to rise in resonance frequency unique to each saturated analyte, the frequency-time trace may be indicative for each chemical. The time response for each analyte absorbed into the polymer coating can be modeled as a solution of the Fick's law of diffusion in terms of a series of exponential terms.^{29,30} To first order approximation, assuming that the resonance frequency shifts are linearly proportional to the ratio of vapors diffused into the polymer at a given time, we model the resonance frequency as an exponential relaxation function³¹ to extract the response time constant, which we define as the time taken to achieve 63% (or 1 - 1/e) of the total frequency shift. Time constants of 8.4, 11.7, and 26.9 s have been measured for the spin coated RMB with the injection of saturated ethanol, water, and benzene vapor into the flow chamber, respectively (see Fig. 3(b)). For the ethanol vapor, we observe that the resonance frequency overshoots, but this effect is not seen for diluted ethanol vapor whose concentration is 2.9 ppt (see Fig. 3(b)) or less.

The relationship between resonance frequency and squeeze film effect in the RMBs is examined. The squeeze film effect governs the gas flow between a microbridge and substrate moving towards each other. If the bridge moves slowly, gas is squeezed out and dissipation loses result. For fast movement, it compresses the air, resulting in spring forces. A characteristic dimensionless squeeze number, σ_{SQN} , can be defined as³²

$$\sigma_{SQN} = \frac{12\mu a^2 \omega}{P_a d^2},\tag{4}$$

where *d* is the distance between the substrate and the resonator, P_a is the ambient pressure, μ is the viscosity of air, ω is the natural frequency, and *a* is the typical dimension (or the width for a doubly clamped beam structure) of the RMB. For low squeeze numbers (and frequencies), the air can flow out from below the resonator without compression and thus there is no significant fluid increase in the device stiffness. On the other hand, at high squeeze numbers, the gas does not have sufficient time to flow out from below the device and the air acts like a compressible spring. The squeeze number for our RMB is estimated to be $\sigma_{SQN} = 0.074 \ll 10$, so that the ambient pressure gas is not trapped under the resonator but readily flows from the compressed area.

The significantly reduced squeeze film damping effect is due to a relatively large gap ($\sim 1.2 \,\mu$ m) between the resonator and the substrate that leads to a higher qualify factor.³³ In Figure 3(a), the functionalized RMB has fundamental mode quality factors of 8.7, 23.7, 26.6, and 28.8 in dry nitrogen, saturated water, benzene, and ethanol vapor, respectively.



FIG. 4. (a) Pressure calibration of the RMB in ambient condition $(\Delta f/\Delta P = -3.86 \pm 0.41 \text{ kHz/Torr})$. (b) Pressure rise per ethanol concentration increase $(\Delta P/\Delta C = 0.36 \pm 0.08 \text{ Torr/ppt})$. (c) Steps of frequency rises upon increase in vapor concentration before and after baseline (dashed line) subtraction, (d) short term frequency fluctuation, Δf_n , or a standard deviation of the frequency changes $(\Delta f_n = \pm 0.25 \text{ kHz})$ in a minute.

This provides an improvement of more than a factor of two in the quality factor in comparison with previous implementations²⁴ in ambient condition because of reduction in energy dissipation of the RMB due to the reduced squeeze film damping. Figure 3(c) shows that despite the decrease in amplitude, as the resonance frequency shifts upward, the quality factors of the resonators scale with resonance frequency as vapors are introduced into the flow chamber, similar to the mechanical behavior in other mechanical resonators in air.^{33,34} This also suggests that the mechanical behavior of the bilayer is strongly dominated by the poly-Si RMB, whereas the PMMA layer serves mostly to introduce stress changes only. The magnitudes of resonance frequency shifts (dry nitrogen, water, benzene, and ethanol by increasing order) and frequency dependence of quality factor have been reproducibly observed in several devices functionalized by the same protocol in our laboratory.

B. Device performance

In order to characterize vapor detection sensitivity of functionalized RMBs, we first consider basic limits on our device performance. One important consideration is the pressure dependence of the RMB's resonance frequency. According to Eq. (5), the squeeze number is very low, which ensures that the RMB is not in the regime where the resonance frequency increases linearly with the pressure.^{34–36} Instead, the resonance frequency decreases in our experiment as the pressure inside the flow cell increases presumably due to mass entrainment.³⁷ For example, Figure 4(a) shows an example of the averaged resonance frequency variations of the RMB due to pressure variations inside the flow chamber. Here, the sign of the frequency change is opposite to that introduced by swelling of the polymer layer. Frequency shift per unit pressure change $(\Delta f / \Delta P)$ is measured to be -3.86 ± 0.41 kHz/Torr, while the temperature is kept stable throughout the experiments. The flow rate of dry nitrogen is fixed as 10 000 sccm for this measurement, which causes an increase in pressure of about 16 Torr inside the flow chamber. However, pressure fluctuation for a nominally constant dry nitrogen flow is found to be 0.32 ± 0.05 Torr as measured for an hour. In addition to the frequency change observed due to the pure pressure variation, we note that due to the imbalance in our flow system there is a small pressure rise per ethanol concentration increase $(\Delta P/\Delta C)$. This is measured to be 0.36 ± 0.08 Torr/ppt (see Fig. 4(b)). Combining these results by multiplying $\Delta f/\Delta P$ with $\Delta P/\Delta C$, the frequency shift per change in ethanol concentration contributed by pressure change, $\Delta f/\Delta C$, pressure, is estimated to be only -1.39 Hz/ppm. It is essential for the RMB to achieve vapor detection sensitivity higher than this value, in order to accurately sense the analyte vapor.

Other important considerations regarding limits on our device performance are baseline frequency drift and fluctuation. The resonance frequency of the RMB surrounded by flowing dry nitrogen gas represents the baseline measurement, which is monitored by a spectrum analyzer with its built-in frequency-sweep source output. The resolution bandwidth and frequency span are set to be 10 kHz and 2 MHz, respectively, which yields about 15 ms of typical integration sweep time for a single frequency-sweep measurement. The spectrum analyzer samples 21 data points for each frequency and averages them, giving approximately 300 ms of overall integration time. Allowing each time interval to be long enough for data acquisition, we record the data every half second. The baseline exhibits a slow but continuous exponential drift with a characteristic time constant that is two orders of magnitude greater than the response time to typical analyte vapors. After the ethanol purge is completed, the overall magnitude of rise in the baseline during the course of the measurement is $\sim 120 \,\text{kHz}$ in average for each run (usually 30 min to 1 h). An example of the natural baseline drift is shown as the dashed line in Figure 4(c). We estimate that this drift in the baseline frequency is due to effects of moisture from the environment, or a slow stress-strain relaxation of the buckled beam. Similar results in the resonance frequency shifts have been obtained for each run in spite of the baseline rises. For further analysis, the exponential baseline is subtracted from the observed resonance frequency. For example, Figure 4(c) shows steps of frequency rises upon the corresponding steplike increase in vapor concentration before and after baseline subtraction.

In addition to the long-term frequency drifts, short-term frequency fluctuation also limits vapor detection resolution of the functionalized RMBs. For instance, Figure 4(d) illustrates an example of such frequency fluctuations. In this figure, the short term frequency fluctuation Δf_n , which represents a standard deviation of the frequency changes in a minute, is measured to be approximately $\Delta f_n = \pm 0.25 \text{ kHz}$. Compared to the width of the resonance frequency Δf_0 $(= \sim 200 \text{ kHz})$, this frequency fluctuation component is very small (that is, ~0.25% of Δf_0). We believe that this frequency variation is mainly due to thermal fluctuations in the polymer coating around the detection laser spot, which adds to other sources of frequency variations. Pressure fluctuations combined with the baseline rise and frequency fluctuation sets the resolution limit of our vapor sensing method with the current gas delivery and readout system.

C. Frequency shift analysis and device sensitivity

Thanks to their dynamic range, PMMA coated RMBs can detect the presence of analyte vapors well below their saturated vapor pressure. According to a simplified model²⁴ of doubly clamped beams under compressive stress, the dependence of the frequency shift on the analyte vapor concentration is approximately

$$\Delta f(C) = \sqrt{\alpha C},\tag{5}$$

where Δf is the resonance frequency shift from baseline, C is the concentration of analyte vapor, and α is the analytedependent hygrometric expansion coefficient of PMMA. Here we assumed linearity between the strain and the stress of hygrometric expansion in the polymer exposed to vapor. Figure 5(a) demonstrates measured resonance frequency shifts in the functionalized RMB of Figures 1 and 2 with fits to Eq. (6) for each analyte. These experimental results agree with the theory of dynamics of buckled beams,^{38,39} showing that the resonance frequency shifts are proportional to the square root of analyte vapor concentration, in the case of the volatile vapors ethanol and benzene. In particular, ethanol showed the highest sensitivity among all analytes for this study. On the other hand, water vapor exhibited weak square-root dependence of resonance frequency shifts with changing concentration. We estimate that these observations



FIG. 5. Response in frequency shift vs analyte concentration after its normalization with vapor pressure (a) in a critically buckled RMB (calculated relieved stress = \sim 59.5 MPa) and (b) in a RMB with initial buckling, which is further from the critical buckling state (calculated relieved stress = \sim 113 MPa).

possibly result from unique complex diffusion mechanism of water in PMMA, which consists of dual mode sorption kinetics present in microvoids due to retarded swelling of the polymer.²⁹

Similar device characteristics have been observed in other spin coated RMBs, proving a reliable device fabrication scheme (see Fig. 1). Figure 5(b) shows corresponding measurements of another functionalized RMB, in which the initial buckling is further from the critical buckling state than the RMB tested in Fig. 5(a). According to Emam *et al.*,⁴⁰ the relieved stress, σ_{rel} , or the difference between the residual stress, σ_{res} , and the critical buckling stress, σ_{crit} , of a beam structure, is given by (see Eq. (A7) in Appendix)

$$\sigma_{rel} = \sigma_{res} - \sigma_{crit} = \frac{\pi^2 E r^2 q_B^2}{4L^2},\tag{6}$$

where q_B is the midpoint elevation of the beam in out-ofplane direction. While calculated relieved stress of the critically buckled RMB is ~59.5 MPa, that of more buckled RMB is ~113 MPa. This increase in the relieved stress leads to the reduced hygrometric expansion coefficient α measured



FIG. 6. (a) Time response of diluted ethanol vapor in ppm range. Response time constant is greater for diluted vapor than saturated vapor. (b) Response in frequency shift vs ethanol concentration in ppm range for the RMB operated near the critical buckling state, 200 s after the ethanol injection $(\Delta f/\Delta C_{ethanol} = \sim 360 \text{ Hz/ppm}).$

in all analytes with corresponding ratios. Despite their different initial buckling states, both RMBs exhibit similar behavior of frequency shifts with introduction of vapors, verifying consistent device operations of the RMB.

With these PMMA-coated RMBs, we have demonstrated detection of ethanol vapors in a few hundred ppm range. Figures 6(a) and 6(b) show experimental resonance frequency shifts of the functionalized RMB as a function of time and ethanol concentration in ppm range, respectively. In this regime, dependence of the frequency shift on the analyte vapor concentration effectively becomes linear, yielding $\Delta f / \Delta C_{ethanol} = \sim 360 \, \text{Hz/ppm}$ to first order approximation after 200 seconds (see Fig. 6(b)). This value is \sim 250 times greater in magnitude than the frequency shift that results solely due to pressure increase induced by ethanol vapor injection into a flow cell ($\Delta f / \Delta C_{, pressure} = -1.39 \, \text{Hz/ppm cal-}$ culated results from Figs. 4(a) and 4(b)). As we consider 500 Hz of the short-term resonance frequency fluctuation, corresponding to Fig. 4(d), it leads to an estimated minimum detectable concentration of ~1.39 ppm of ethanol vapor (500 Hz/360 Hz/ppm = 1.39 ppm). With a more sensitive detection scheme than the one used in the current experiment, together with more stable baseline frequencies over time under stabilized conditions, the sensitivity of our RMB could potentially be enhanced.

IV. CONCLUSION

In summary, we have demonstrated that resonance frequency shifts for PMMA functionalized stress-based resonant volatile gas microsensors, operated near their critically buckled point, can be used in chemical sensing applications. The microsensors exhibit high sensitivity and dynamic range (as large as 150% frequency shifts) enabled by operation near the critical buckling stress with rapid frequency response due to the swelling of the thin polymer coating, effectively increasing surface-to-volume ratio and thus promote faster polymer swelling response. In addition to fast response and high dynamic range, significant improvements in the quality factor of the microsensors in ambient condition were achieved and sensing with the RMB of individual volatile vapors has been demonstrated. The standard microfabrication procedure of doped poly-Si RMBs suggests that the miniaturized microsensors are comparable with electrical detection implemented by complementary metal-oxide-semiconductor (CMOS) based electronics⁴¹ and could be integrated with surface functionalization. Microsensors coated with a high yield functionalization polymer surface can improve their sensitivity, provided that the RMB is pre-stressed closer to its critical buckling. In addition we anticipate that reduction of thermal noise (by use of all-electric detection), and further evolved functionalized coatings will result in higher sensitivity to specific analytes. The mechanism of the stressoptimized doubly clamped beam resonator with surface functionalization is of interest for real-time volatile-organic-compound ambient gas sensing in applications of breath analysis for trace vapors, biomedical, clinical, and military applications.

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APPENDIX: FUNDAMENTAL FREQUENCY OF A BUCKLED BEAM

In order to highlight the main ideas beyond the operational principle of the microsensor, we first consider the resonance behavior of the pre-buckled beam and, specifically, the influence of the axial compressive force on the fundamental frequency of the device. The dynamics of free undamped vibrations of the beam, considered in the framework of the Euler-Bernoulli theory, are governed by the equation

$$EI\frac{\partial^4 \hat{z}}{\partial \hat{x}^4} + \left[\hat{P} - \frac{EA}{2L} \int_0^L \left(\frac{\partial \hat{z}}{\partial \hat{x}}\right)^2 d\hat{x}\right] \frac{\partial^2 \hat{z}}{\partial \hat{x}^2} + m_l \frac{\partial^2 \hat{z}}{\partial \hat{t}^2} = 0. \quad (A1)$$

Here $\hat{z}(\hat{x}, \hat{t})$ is the deflection of the beam (the elevation with respect to its straight stress-free state), \hat{x} and \hat{t} are the coordinates along the beam and time, respectively, L is the length of the beam, m_l is the mass per unit length, E is the Young's modulus, and \hat{P} is the applied compressive axial force. In addition, I and A are the area moment inertia of the cross-section and the cross-sectional area of the beam, respectively. Equation (A1) is completed by the boundary conditions corresponding to the fixed (in both x and z directions) ends of the beam. The non-dimensional, more convenient for the analysis, counterpart of Eq. (A1) is³⁸

$$z^{IV} + \left[4\pi^2 P - \frac{1}{2}\int_0^1 (z')^2 dx\right]z'' + \ddot{z} = 0.$$
 (A2)

Here

$$z = \frac{\hat{z}}{r}, \quad x = \frac{\hat{x}}{L}, \quad t = \hat{t}\sqrt{\frac{EI}{m_l L^4}}, \quad P = \frac{\hat{P}L^2}{4\pi^2 EI}, \quad r = \sqrt{\frac{I}{A}}.$$
(A3)

One observes that the deflection of the beam is normalized by the gyration radius *r* of the cross-section and the compressive axial force \hat{P} is normalized by the Euler's buckling force of a double-clamed beam $P_E = 4\pi^2 EI/L^2$. Note that the natural frequencies and natural modes of the beam pre-buckled by the force P > 1 were analyzed in Nayfeh *et al.*³⁸ However, the exact characteristic equation used for the calculation of the natural frequencies is cumbersome and difficult for analysis. Here we present a simple, based on the Galerkin decomposition, approximation allowing estimation of the frequency and illustrating the influence of the axial stress on the spectral characteristics of the beam. Since P > 1, we represent the elevation of the beam in the form

$$z(x,t) = z_B(x) + w(x,t),$$
 (A4)

where $z_B(x)$ represents the buckled shape of the beam and w(x, t) is the deflection with respect to the buckled shape. We substitute Eq. (A4) into Eq. (A2), linearize the resulting equation for $\max_{x \in [0,1]}(w) \ll 1$, and take into account that $z(x) = z_B(x)$ satisfies the static counterpart of Eq. (A2). Then, we obtain

$$w^{IV} + \left[4\pi^2 P - \frac{1}{2}\int_0^1 (z'_B)^2 dx\right]w'' - \left(\int_0^1 z'_B w' dx\right)z''_B + \ddot{w} = 0.$$
(A5)

In the framework of the single degree of freedom approximation, we set

$$z_B(x) \approx q_B \phi(x), \quad w(x,t) \approx q \psi(x) e^{i\omega t}.$$
 (A6)

Here we define $\phi(x) = [1 - \cos(2\pi x)]/2$ is the first buckling mode of the beam³⁸) while $\psi(x)$ is the base function and ω is the corresponding natural frequency of the beam. And

$$q_B = 4\sqrt{P-1} \tag{A7}$$

is the midpoint elevation of the beam in the post-buckled configuration. Substituting Eq. (A6) into Eq. (A5), multiplying it by $\psi(x)$, integrating by parts and taking into account fixed boundary conditions yield the eigenvalue problem

$$\begin{cases} \int_0^1 (\psi'')^2 dx - \left[4\pi^2 P - \frac{1}{2} q_B^2 \int_0^1 (\phi')^2 dx \right] \int_0^1 (\psi')^2 dx \\ + q_B^2 \int_0^1 \phi' \psi' dx \int_0^1 \phi' \psi' dx - \omega_1^2 \int_0^1 (\psi)^2 dx \end{cases} q = 0.$$

The lowest natural frequency of the buckled beam ω_I is therefore given by the expression

$$\omega_{1} = \sqrt{\frac{\int_{0}^{1} (\psi'')^{2} dx - 4\pi^{2} P \int_{0}^{1} (\psi')^{2} dx + q_{B}^{2} \left[\frac{1}{2} \int_{0}^{1} (\phi')^{2} dx \int_{0}^{1} (\psi')^{2} dx + (\int_{0}^{1} \phi' \psi' dx)^{2}\right]}{\int_{0}^{1} (\psi)^{2} dx}.$$
(A8)

We use the first buckling mode of the beam as the base function, i.e.,

$$\psi(x) = \phi(x) = \frac{1}{2} [1 - \cos(2\pi x)], \tag{A9}$$

and obtain

$$\omega_1 = \sqrt{\frac{b - 4\pi^2 P s + \frac{3}{2}s^2 q_B^2}{a}} = \omega_1^0 \sqrt{1 - 4\pi^2 P \frac{s}{b} + \frac{3}{2} \frac{s^2}{b} q_B^2},$$
(A10)

where the coefficients

$$b = \int_0^1 (\phi'')^2 dx = 2\pi^4, \quad s = \int_0^1 (\phi')^2 dx = \frac{\pi^2}{2},$$

$$a = \int_0^1 \phi^2 dx = \frac{3}{8}$$
(A11)

are associated with the bending, stretching stiffness, and the mass of the beam, respectively. And $\omega_1^0 = \sqrt{b/a} = 4\pi^2/\sqrt{3}$ is the Rayleigh quotient approximation of the fundamental mode frequency of the beam without axial force. Note that $\omega_1^0 = 22.792$ while the exact value is $4.73^2 = 22.373$. By substituting Eq. (A11) into Eq. (A10) and taking into account the expression for q_B , Eq. (A7), we obtain

$$\omega_1 = \omega_1^0 \sqrt{2(P-1)}$$
 (A12)

or, taking into account Eq. (A7)

$$\omega_1 = \frac{\omega_1^0 q_B}{2\sqrt{2}}.\tag{A13}$$

Equation (A13) indicates that in the framework of the single mode approximation the frequency of the buckled beam is a linear function of the midpoint elevation of the beam. Comparison between Eq. (A12) and the exact result given in Nayfeh *et al.*³⁸ shows that the relative error in the frequency is 4.8% for P = 2 (which corresponds to $q_B = 4$ or to the midpoint deflection to the thickness ratio of $\hat{q}_B/d = 2/\sqrt{3}$).

Note in passing that in the pre-buckling case P < 1 the expression for the fundamental frequency ω_1 of the straight beam can be obtained from Eq. (A10) by setting $q_B = 0$, which yields the value $\omega_1 = \omega_1^0 \sqrt{1 - P}$. One can conclude therefore that the sensitivity of the resonance frequency to the axial force in the buckled configuration is higher than that in the pre-buckled case.

The fundamental frequency of microbridges in the first buckled configuration f_0 can therefore be approximated by the expression

$$f_0 = 2\pi \sqrt{\frac{2EI}{3m_l L^4} \left(\frac{\sigma}{\sigma_E} - 1\right)},$$
 (A14)

where σ is the axial compressive stress and $\sigma_E = 4\pi^2 E r^2 / L^2$ is the Euler's buckling stress.

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