Femtogram mass detection using photothermally actuated nanomechanical resonators

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Nanomechanical devices with very small mass and size have the potential for mass sensing at the level of individual molecules. In the present study, we designed nanomechanical mass sensors, demonstrated their operation under ambient pressure and temperature, and achieved femtogram-level mass sensitivity. Our nanomechanical resonators were gold-coated silicon cantilevers with resonance frequencies in the range of 1 to 10 MHz, characteristic thicknesses of 50–100 nm, and force constants of about 0.1 N/m. Using a cantilever with a resonant frequency of 2.2 MHz that was excited photothermally, we measured a mass change of 5.5 fg upon chemisorption of 11-mercaptoundecanoic acid. Our analysis indicates that, by decreasing the mass of the cantilever and increasing the excitation amplitude, even higher mass sensitivity can be realized in an easily accessible frequency range (<100 MHz). © *2003 American Institute of Physics.*
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Anticipated applications of nanotechnology are vast, and they include the possibility to address many challenges of chemical, environmental, and biological analysis. One of the approaches to implement this possibility is associated with the use of nanomechanical resonators that may function as ultrasensitive transducers.[1,2] Micromechanical and electromechanical resonators, such as flexural plates, quartz crystal microbalances and surface acoustic wave devices have already found numerous applications as mass sensitive transducers[3] in chemical and biological sensors. It is important to note that sensor designs based on these electromechanical transducers have been thoroughly refined over several decades and the demonstrated figures of merit closely approach their theoretical limitations.[4] In the case of cantilever resonators, however, dramatic improvements in analytical figures of merit can be achieved merely by scaling their sizes down to the nanoscale. Predictions of mass sensitivities at the level of individual molecules are especially intriguing.[5] A series of more recent studies demonstrated, both theoretically and experimentally, that smaller cantilever transducers have indeed significantly improved performance in terms of minimum detectable force[6] and mass.[7–9]

In our previous work, we used cantilevers in both resonance[10] and static deflection modes.[11] By using either standard or modified microcantilevers, we have measured optical,[12] chemical,[13] and fluidic[14] stimuli. In the present work, we explore the opportunity to develop nanosized mechanical structures that exhibit ultrahigh mass sensitivity, ultimately approaching detection of various analytes at the level of a single molecule. In addition to analytical implications, single-molecule detection is also very important for many fundamental areas of physics, chemistry, and biology.[15] By using photothermal laser actuation and interferometric read-out, we were able to measure resonance frequency shifts that accompany the chemisorption of 11-mercaptoundecanoic acid on the surface of gold-coated cantilevers. Binding of thiol molecules with a total mass of a few femtograms could be monitored in air. Comparable mass sensitivity achieved experimentally using cantilever-type transducers in vacuum has been reported recently.[16]

The as-supplied cantilevers (200 μm long, 50 μm wide, and 1.5 μm thick) were coated with a 35-nm gold layer on one side to increase optical reflectivity and response to photothermal actuation. Using an focused ion beam (FIB) milling instrument (FEI 200), we obtained cantilevers that measured 2 to 6 μm long, 50 to 100 nm thick, and had resonance frequencies in the range of 1 to 6 MHz (Fig. 1). The experimental setup used in our measurements (Fig. 2) consisted of optical components for interferometric readout and photothermal actuation of cantilevers, a vacuum-compatible cell, a high-speed avalanche photodiode (APD) detector, and a network analyzer (HP4195A). Interferometric readout included a 3-mW HeNe laser, a beam expander, a spatial filter, a 50%/50% cube beam splitter and a 50× microscope objective lens. The interferogram was focused on the APD detector which had an integrated transimpedance amplifier. Photothermal actuation of the cantilevers was provided by a 4-mW modulatable diode laser (wavelength of 670 nm) focused on the cantilever and driven by the output signal from the network analyzer.

In order to measure adsorbate-induced changes in the cantilever resonance frequencies, cantilevers were mounted in an open cell which was equilibrated with ambient air and permitted exposure to vapors of volatile analytes, small amounts of which could be placed in proximity to the cantilever. Alternatively, the cell could be connected to a vacuum line equipped with a thermocouple vacuum gauge and a mechanical vacuum pump.

We found that all our fabricated resonators exhibited very similar normalized widths of the resonances in air, which were almost independent of the cantilever thicknesses and shapes. A possible explanation of this observation is that, for the cantilevers in air, viscous damping by the medium is the predominant energy dissipation mechanism. Based on the

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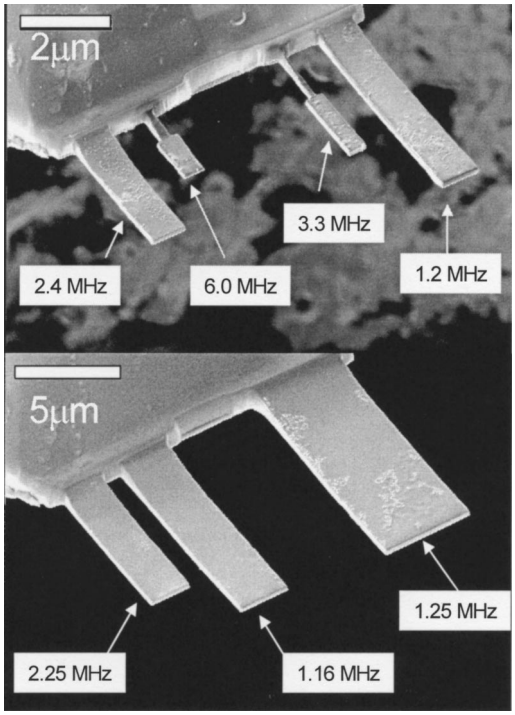

FIG. 1. Ion scanning micrograph obtained using an FIB instrument. Conventional Si microcantilevers were used in these studies as a starting material for FIB milling in order to create much smaller cantilevers with resonance frequencies in the range of 1 to 10 MHz. Approximate values of the resonance frequencies are indicated for each cantilever.

width of the measured resonance curves, a Q-factor of 25 was estimated. In order to verify whether viscous damping by the medium rather than intrinsic mechanical losses was responsible for the low Q-factor, we measured cantilever resonances at reduced pressures. We observed changes in the shape and position of the resonance curve when we lowered the cell pressure from ambient down to 0.7 Pa. The measured resonance curve exhibited at least a fivefold increase in the Q-factor. A very important conclusion that can be drawn from these observations is that minimization of intrinsic mechanical losses may not be practical in the case of nanomechanical mass-sensitive transducers operating in air at room temperature and atmospheric pressure.

We used a rectangular gold-coated silicon cantilever with a resonance frequency of 2.25 MHz with approximately 2 μm width and 6 μm length and exposed it to 11-mercaptoundecanoic acid vapor. We measured the resonance frequency of the cantilever mounted in an open cell both before and after exposure to vapors of 11-mercaptoundecanoic acid. Adequate vapor pressure was generated by heating small amounts of powdered analyte to 60 °C. Upon exposure of the cantilever to 11-mercaptoundecanoic acid vapors, the resonance frequency underwent a readily measurable resonance frequency shift (Fig. 3), attributable to chemisorption of the analyte molecules onto the gold-coated surface of the cantilever. In order to estimate an additional cantilever mass due to attached 11-mercaptoundecanoic acid molecules, we used a model of a weakly damped resonator:[17]

$$\Delta m = G\frac{k}{\pi^2}\left(\frac{1}{f_1^2}-\frac{1}{f_0^2}\right) \simeq 2G\frac{k}{\pi^2}\frac{\Delta f}{f_0^3}, \tag{1}$$

where f_0 and f_1 are, respectively, the cantilever frequency before and after chemisorption of thiol molecules, k is the spring constant of the cantilever, $G(\approx 1.37)$ is a geometrical factor of the cantilever, and the frequency instability is $\Delta f = f_0 - f_1$. Based on the resonance frequency shift $\Delta f = 2$ KHz (shown in Fig. 3) and using Eq. (1), we found the added mass to be 5.5×10^{-15} g. This value is very close to a 50% coverage of a monolayer of 11-mercaptoundecanoic with a total mass of 6×10^{-15} g over the area of the cantilever, which is 12 μm^2.

In our efforts to estimate the threshold of mass sensitivity for cantilever resonators, we explored two different approaches. In the first approach, an assumed frequency instability $\Delta f = (f_1 - f_0)$ was substituted into Eq. (1). A ratio of $\Delta f / f_0 = 10^{-4}$ is a reasonable assumption for the relative resonance frequency instability in the case of cantilevers with moderate to low mechanical quality factors ($Q < 1000$). In order to investigate the effect of geometrical scaling, we assumed a fixed cantilever length-to-width ratio of 3:1, while cantilever thickness varied to satisfy the requirement of a fixed force constant of 0.1 N/m. Our calculations of resonance frequencies and force constants were based on the classical models of rectangular thin plates.[18] These assumptions allowed us to predict mass sensitivity of the fabricated nanomechanical resonators (see Fig. 4). As can be seen in Fig. 4, femtogram-level sensitivities can be achieved using cantilevers with resonance frequencies in the range of 1 to 5 MHz. Our second approach in predicting cantilever mass sensitivity accounts for the fundamental factors that limit resonance frequency stability. As it was discussed previously,[8,19,20] the noise due to thermal excitation (i.e., continuous exchange between thermal and mechanical energy of the oscillator) imposes an absolute theoretical limit on the frequency stability and, in turn, threshold mass sensitivity of any nanomechanical resonator. Therefore, the minimum detectable mass Δm_{th} can then be expressed as

$$\Delta m_{\mathrm{th}} = \frac{8G}{\langle z^2\rangle^{1/2}}\frac{m_0^{5/4}}{k^{3/4}}\sqrt{\frac{k_{\mathrm{B}}TB}{Q}}, \tag{2}$$

where k_{B} is the Boltzmann constant, T is the temperature of the cantilever, B is the bandwidth of the measurement, k is the cantilever force constant, Q is the mechanical quality

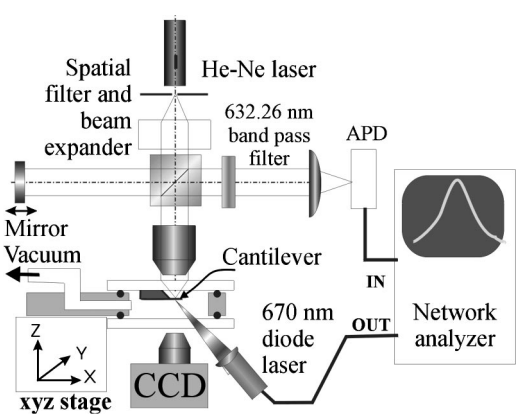

FIG. 2. Schematics of the experimental setup for photothermal actuation and interferometric readout of the FIB modified cantilevers.

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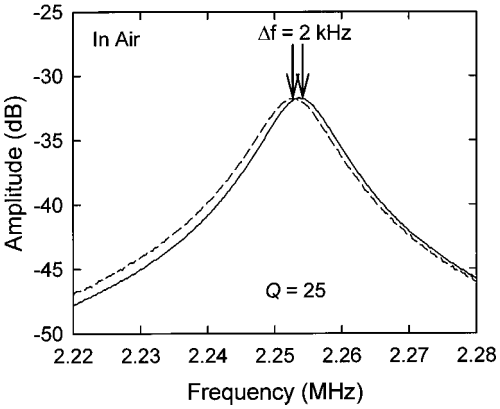

FIG. 3. A frequency shift in the cantilever resonance curve was observed after adsorption of 11-mercaptoundecanoic acid under ambient conditions. The measure frequency shift corresponds to an added mass of 5.5 fg. The experiments were conducted at ambient temperature and pressure.

factor, m_0 is the initial cantilever mass, and $\langle z^2 \rangle^{1/2}$ is the root-mean-square amplitude of the cantilever motion. According to Eq. (2), the thermally limited mass sensitivity threshold is adversely affected by a low Q-factor. Nevertheless, the other design and operation parameters can be tailored to compensate for the higher susceptibility of lower Q-factor nanomechanical resonators to thermally induced noise.

We would like to point out that mass detection thresholds predicted according to our first approach (solid line in Fig. 4) closely approach the thermally limited thresholds calculated for $Q=25$ and $z_{\max}$ $(=\langle z^2 \rangle^{1/2})=0.6$ nm (upper dashed line in Fig. 4). However, thermally limited mass detection thresholds can be lowered by two orders of magnitude (lower dashed curve in Fig. 4) when the amplitude of cantilever oscillation increases from 0.6 to 60 nm. The mass change due the presence of chemisorbed molecules detected in our experiments was 5.5×10^{-15} g (solid square in Fig. 4), and corresponds to a relative frequency deviation of $\Delta f/f_0=9\times10^{-4}$. Although the latter value for $\Delta f/f_0$ is not the limit of our measurement, it is an order of magnitude greater than the relative frequency instability of $\Delta f/f_0=10^{-4}$, which we assumed in our analysis (solid line in Fig. 4). The value of $\Delta f/f_0=10^{-4}$ agrees well with the thermomechanical limit for a cantilever with $f_0=2.25$ MHz, $Q=25$ and $\langle z^2 \rangle^{1/2}=0.6$ nm and yields a mass detection threshold of 5.7×10^{-16} g (solid circle in Fig. 4). By using some of the smaller cantilevers shown in Fig. 1 and/or increasing the amplitude of excited oscillations, we expect to further improve the mass detection threshold.

While fabrication, operation, and read-out of gigahertz devices remain challenging, we demonstrated that femtogram-level mass sensitivity is possible under ambient conditions using cantilevers with much lower resonance frequencies (1–10 MHz) and can be fabricated and operated in air.

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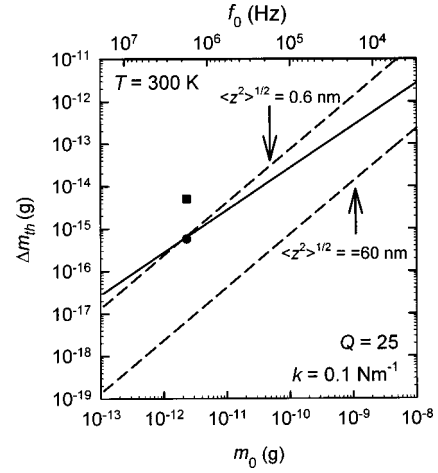

FIG. 4. Comparison of mass detection thresholds for a resonating rectangular Si cantilever with $k=0.1$ N/m defined by a fixed frequency instability of 10^{-4} (solid line) and by the cantilever intrinsic thermal noise (dashed lines). Thermally limited mass-detection thresholds are calculated for the two cases: (i) $z_{\max}(=\langle z^2 \rangle^{1/2})=0.6$ nm, $Q=25$, that is, weakly excited resonator (upper dashed line) and (ii) strongly excited resonator with $z_{\max}=60$ nm, $Q=25$ (lower dashed curve). The experimentally measured mass change (solid square) is approximately 10 times larger than the mass-detection threshold (solid circle) calculated for the cantilever with $f_0=2.25$ MHz used in our experiments.

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