Mass sensing of adsorbed molecules in sub-picogram sample with ultrathin silicon resonator

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Ultrathin single-crystalline silicon cantilevers with a thickness of 170 nm as a resonating sensor are applied to mass sensing. The hydrogen storage capacity of a small amount of carbon nanotubes (CNTs), which were mounted on an ultrathin resonator by a manipulator, is measured from the resonant frequency change. The resonator is annealed in ultrahigh vacuum to clean the surface and increase the quality factor, and exposed to oxygen gas to oxidize the surface for long-term stability. The resonator can be electrostatically actuated, and the vibration is measured by a laser Doppler vibrometer in ultrahigh vacuum. The mass of the CNTs is determined by the difference of resonant frequencies before and after mounting the CNTs, and the hydrogen storage capacity is determined from the frequency change after exposure to high-pressure hydrogen as well. The obtained hydrogen storage capacitance is 1.6%–6.0%. The available mass resolution and the achieved stability of the resonance of the 170-nm-thick resonator are below 10^{-18} g and 5 Hz/days, respectively. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1536262]

I. INTRODUCTION

Nanoscience and engineering tools, typified by scanning probe microscopy (SPM), are significantly increasing the importance for nanotechnology. Micromachined resonating sensors play an important role for sensing a small interaction force between a tip and a surface as much as 5.6×10^{-18} N,[1] as well as for a mass sensor with a sensitivity of 10^{-12} g.[2] A number of applications, such as force microscopy,[3,4] magnetometry,[5,6] and charge detection[7,8] stimulate continuous efforts to improve the performance of oscillators.

From scaling law, it is expected that the sensitivity of the resonating sensor increases by further miniaturization. Up to now, we have developed the fabrication technique and characterized the mechanical properties of ultrathin single-crystalline silicon cantilevers down to 60 nm in thickness.[9] As a result, the quality factor (Q factor) of the cantilever beam was decreased with decreasing the thickness.[10,11] It is a serious problem to increase the sensitivity. However, it was found that the cleaning of the cantilever by flash annealing in ultrahigh vacuum (UHV) to remove the natural oxide on the surface could dramatically increase the Q factor.[12]

On the other hand, a mass sensor to detect nanogram mass changes is one of the important applications of the micromachined cantilevers. It is known that there are two kinds of sensing methods of molecules or atoms as a very sensitive chemical sensor or mass sensor; one is to detect the static bending caused by surface stress due to analyte absorption onto a flexible cantilever on which chemical active layer is coated.[13,14] This method is believed to be very sensitive, however, quantitative evaluation is difficult because the stress induced by the adsorption is unpredictable. Furthermore, the drifts of the signal caused by the optical sensing system make long-time measurements difficult. The other method is to use resonant frequency changes due to mass loading;[14–16] it especially seems to be effective when mass loading does not cause surface stress. Many efforts have been done to raise the sensitivity of the resonating mass sensor,[17] however, it has never be used to measure adsorption characteristics on a solid to our knowledge. Undesired effects that cause the drift of the resonant frequency, like contamination, mechanical instability, and temperature change, should be avoided as much as possible. Our cantilevers are designed to aim for extreme sensitivity, and measurements were done in UHV to achieve extreme stability by eliminating contaminated adsorption such as water molecules, which enable us to measure mass changes below picograms of weight with high precision.

On the other hand, recently, carbon nanotubes[18] have attracted attention for application of fuel cells with the capability of reversible hydrogen storage as a clean energy source. The carbon nanotube has a structure in which a graphene sheet is rolled into a tube. A number of publications are devoted to the experimental and theoretical study of gas adsorption on different adsorbent structures. Dillon *et al.* measured the hydrogen adsorption over 10 wt % in carbon nanotubes by temperature programmed desorption (TPD).[19] This article triggered the following studies and verifications by many researchers. The results are still controvertible and most of the reports denied the large storage capacity at room

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TABLE I. Summary of measurement results.

	Size of cantilever beam (μm) (width×length×thickness)	Estimated Spring constant (N/m)	Resonant frequency before mass loading (Hz)	Resonant frequency after mass loading (Hz) (corresponding mass g)	Resonant frequency after hydrogen adsorption (corresponding mass and storage capacity)	Frequency stability (Hz/day)
Sample No. 1	6×48×0.17	0.011	102 410	101 740 3.65×10^{-13}	101 700 3.87×10^{-13} (6.0%)	3
Sample No. 2	6×50×0.17	0.009	95 101	92 240 1.59×10^{-12}	92 195 1.61×10^{-12} (1.6%)	5
Sample No. 3	6×49×0.17	0.010	99 750	98 305 0.67×10^{-13}	98 250 0.70×10^{-13} (3.8%)	1

temperature.[20] In Dillon's report, they used diluted single-walled carbon nanotubes, so the analysis required a large correction. Some reports suggested that the capacity depends on the structure,[21,22] for example, it is considered that open-ended carbon nanotubes have a higher storage capacity because hydrogen can be adsorbed on both the outer and inner sides of the tubes. Because of the difficulties of elaboration and purification, the nanotube samples used in the experimental investigations are not of high purity, containing amorphous carbon and several impurities.[23]

This article describes the ultrasensitive mass sensing that provided the method to investigate a small amount of adsorption of gases onto small quantities of a sample below a subpicogram of weight and demonstrated the measurement of mass change in carbon nanotube bundles due to hydrogen adsorption.

First, we will consider the behavior of an oscillating cantilever sensor. The spring constant k of a rectangular cantilever beam is given by $k=Ewt^3/4l^3$, where E is Young's modulus, and w, t, l are the width, thickness, and length of the cantilever beam, respectively. The fundamental resonant frequency is given by $f_0=0.162t/l^2(E/\rho)^{1/2}$. Mass loading Δm reduces the frequency to f', which is given by

$$\Delta m=\frac{k}{4\pi^2}\left(\frac{1}{f'^2}-\frac{1}{f_0^2}\right). \tag{1}$$

If the mass change is sufficiently small, the frequency change ($\Delta f=f_0-f'$) versus the mass change can be approximated as follows:

$$\frac{\Delta f}{\Delta m}\approx\frac{2\pi^2 f_0^3}{k}. \tag{2}$$

Equation (2) suggests that a large resonant frequency and a small spring constant, i.e., a smaller and thinner resonator, can lead to a more sensitive response.

In our experiment, (100)-oriented silicon cantilevers (resonator) with a thickness of 170 nm, width of 6 μm, and length of 48–50 μm were used. The calculated spring constants and resonant frequencies of each beam are summarized in Table I. The detail of the fabrication sequence of the cantilevers is described elsewhere.[9] The fabricated cantilevers were introduced into an UHV chamber and flash annealed at about 1000 °C by flowing a current into the silicon base supporting the cantilevers at a base pressure of 2×10^{-8} Pa. The temperature was measured by a pyrometer. After this treatment, the measured Q factor in UHV was increased up to about 200 000. To stabilize the resonance, the surface of cantilever was oxidized by exposure to oxygen, and the cantilever was reintroduced into the measurement chamber. After about 1 week leaving the cantilever in UHV, the Q factor decreased down to about 50 000.

The experimental setup for measuring the mechanical response of the resonator is shown in Fig. 1. The measurement system was installed in a clean room of which the temperature was kept almost constant to minimize the frequency drift of the resonator. All measurements were performed in the UHV chamber with a pressure of 1×10^{-7} Pa. The vibration of the resonator was measured through an optical window by a laser Doppler vibrometer that was mounted on a microscope. A metal plate was put on the optical window to actuate the cantilever with electrostatic force by applying a voltage between the cantilever beam and the metal plate. The focal spot size and power of the laser Doppler system were 1–2 μm and 1 mW, respectively. To ensure the self-oscillation of the cantilever by electrostatic force, an actuation signal was applied to the metal electrode from the Doppler signal through a phase adjuster, a band path filter, and a wave converter to rectify the sine signal to rectangular. The oscillation frequency of the cantilever was detected by a pulse counter (Advantest R5363; the frequency

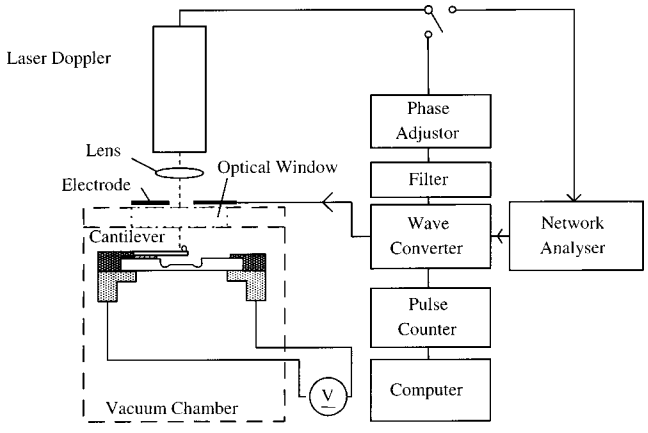

FIG. 1. Experimental setup of the vibration measurement system.

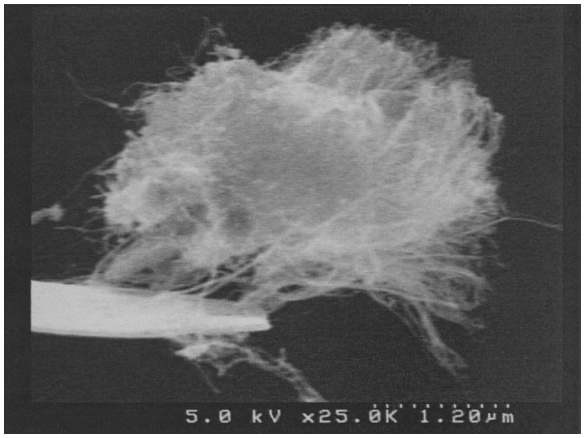

FIG. 2. Typical scanning electron microscopy image of the carbon nanotube bundle attached on the end of the cantilever.

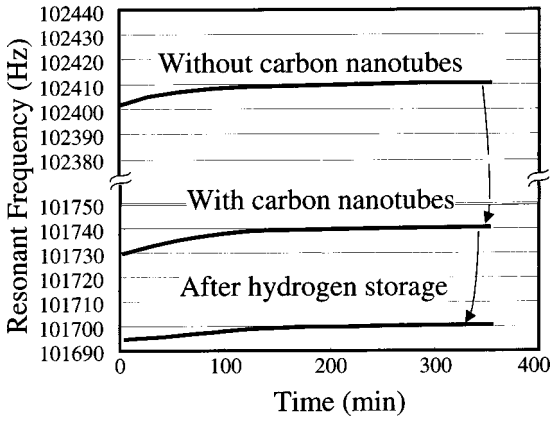

FIG. 4. Resonant frequency changes of the resonator.

stability is about 0.025 Hz/day). To measure the mechanical response spectra, a network analyzer was used. The temperature of the stage holding the cantilever was measured by a thermocouple, and the resonant frequency change due to the temperature change was compensated during the measurements.

The carbon nanotubes used in this experiment were synthesized by hot-filament chemical vapor deposition using a mixture of acetylene and hydrogen gases on a silicon wafer that is catalyzed by iron.[24] Some carbon nanotube bundles are grown on the wafer. Measurements with scanning probe microscopy show that the diameters of most of the carbon nanotubes range between 2 and 8 nm. Using the SPM, one bundle was trapped by scratching mechanically with a sharp tip, and mounted onto the end of a target cantilever with manipulation, as shown by the typical image of a bundle in Fig. 2.

The measurement procedure is shown in Fig. 3(A). The sample was annealed at 1000 °C in nitrogen to remove contaminated adsorbates. In Fig. 3(B), the cantilever without the carbon nanotubes was transferred into UHV through a load-lock chamber, and the resonant frequency was measured for about 6 h using the measurement system until the frequency reached a stable value. In Fig. 3(C), the cantilever was taken out from the measurement system, and the carbon nanotube bundle was mounted on the cantilever. In Fig. 3(D), the cantilever was transferred into the measurement system and the frequency change (mass of the bundle) was measured. In Fig. 3(E), the cantilever was again taken out from the measurement system, and immediately transferred into a high-pressure vessel. The sample was exposed to pure hydrogen (99.999%) with the pressure of 15 MPa for about 1 h at room temperature, and in Fig. 3(F), again transferred into the measurement system and the frequency was measured.

The cantilever was vibrated with electrostatic force by applying a voltage of 5 V between the electrode and the cantilever. The vibration amplitude was kept at about 0.5 μm to prevent the frequency change originated in the amplitude change. Figure 4 shows the typical result of the measurements; the frequency changes of the unloaded, the loaded oscillating cantilever, and after hydrogen storage. It can be seen that the resonant frequencies are slightly increasing and reach to an almost stable value after 2–3 h since put into UHV. Adsorbed contaminations such as water molecules are desorbed in the UHV, which result in stabilizing the resonant frequency. Using Eq. (1), both masses of the carbon nanotube bundles before and after hydrogen storage are calculated and from these differences the hydrogen storage capacity can be estimated. Finally, after removing the carbon nanotube bundle using the manipulator, the resonant frequency was again measured to ensure that the resonant frequency shift was negligible in a series of the experiment. We found the resolution of mass to be about 5×10^{-18} g using the 170-nm-

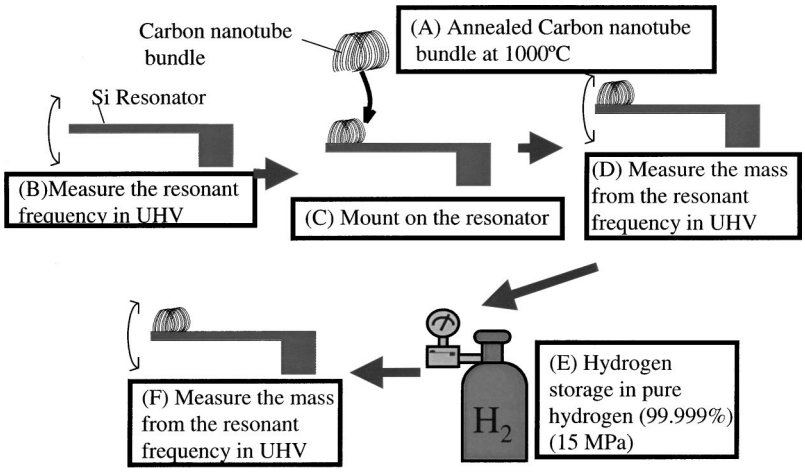

FIG. 3. Schematic procedure of hydrogen adsorption measurement using the resonating mass sensor.

thick cantilever from the noise level (~0.001 Hz).

The measurement results performed on the same carbon nanotube bundle with different masses are summarized in Table I. These samples show different hydrogen storage capacities from 1.6%–6.0%. These errors may be caused by adsorption of airborne particles from ambient air during transfer from the UHV chamber to the high-pressure vessel. Ideally, all experiments should be performed in a vacuum without exposure to air to prevent adsorption of gas molecules onto the cantilever in the future.

In summary, the ultrathin cantilevers show very high stability in UHV by annealing and following oxidation. Using these cantilever beams, a mass sensitivity of about 5×10^{-18} g and stability of 2–3 Hz/day were obtained. Measurements of hydrogen storage capacity on carbon nanotube bundles with masses of 10^{-12}–10^{-13} g were demonstrated. In these measurements, the stability of the resonance limited the measurable mass changes. We believe that this technique will provide a new sensing method to investigate the adsorption characteristics of nanoscaled materials, and further improvements of the resonating sensor will make ultimate sensing enabled to measure the adsorption characteristics of even only one nanostructure and reveal the relationship between adsorption characteristics and structures.

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