POROUS SILICON RESONATORS FOR SENSITIVE VAPOR DETECTION

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ABSTRACT

Common top-down processing techniques were used to fabricate porous silicon resonant mass sensors, allowing for microscale devices with nanoscale features. Porous resonators have an increased surface area for molecular binding and therefore offer improved sensitivity to chemical vapor when compared to non-porous resonators. The porous resonators showed up to 99% improvement in sensitivity to isopropyl alcohol over non-porous resonators fabricated in the same process.

INTRODUCTION

Micro- and nanometer scale resonators have been explored as highly sensitive mass sensors. Binding events on the surface of a resonator alter the mechanical stress and total mass of the resonator. This allows for measurement of the adsorbed mass via a shift in resonant frequency. Scaling the devices to smaller size increases the relative mass change of adsorbed species, thus improving the sensitivity of the devices as mass sensors [1]. A variety of methods have been developed to improve the sensitivity of these resonant sensors, including treatments of sensor surfaces to improve the quality factor [2,3], modifications of readout schemes to measure the sensors more efficiently [4], and materials for decreased energy dissipation and improved robustness [5,6]. To date, porous silicon has been investigated for applications including enhanced sensitivity of pressure sensors via a reduced Young's modulus [7] and detection of chemicals via changes of electronic [8] and optical characteristics [9]. This work focuses on using the large internal surface area of porous silicon for sensitivity enhancement in resonant mass sensors.

Porous materials have previously been coated on the surface of resonators to increase the surface area of adsorption. As previously mentioned, nanomechanical resonant sensors with dimensions in the submicron regime have also been employed as tools to offer impressive mass sensitivity by increased surface area-to-volume ratios. Both scaling and the addition of surface coatings can add complexity to fabrication and readout, whereas nanoscale sensitivity from widely available microscale fabrication techniques can be achieved in the approach described here, where the entire resonant structure is fabricated of porous silicon.

FABRICATION PROCESS

We have designed and fabricated torsional beam resonant gas sensors using surface micromachining process as shown in Figure 1. We simultaneously fabricated porous and non-porous silicon resonators on the same silicon wafer to quantify the sensitivity enhancement. Fabrication started with 4 in. (100) silicon wafers, followed by depositions of 470-nm-thick silicon dioxide serving as a sacrificial layer and 470-nm-thick polysilicon by LPCVD (Tystar Titan II furnace). The structures of the resonators were then defined by photolithography (KarlSuss MA-6 aligner) and deep reactive ion etcher (SLR 770 ICP). Electroless metal-assisted etching of the silicon surface was used to porosify the silicon structures [10]. A 5-nm-thick Au layer was deposited by e-beam evaporation (CHA Mark 40) in order to form thin Au clusters, which served as catalysts for silicon etching. Silicon molecules underneath Au clusters were etched away in an etching solution (49% HF, 30% H₂O₂, and H₂O with a volume ratio of 1:5:10) for 20 seconds. The remaining Au

Figure 1. Fabrication process for a porous silicon resonator. (a) deposition of SiO₂ and polysilicon by LPCVD. (b) photolithography and polysilicon etching by DRIE. (c) Au catalyst layer deposition by E-beam evaporator. (d) porous silicon etching and Au layer removal. (e) sacrificial layer etching and drying with CPD.. Steps (c) and (d) are omitted for non-porous silicon resonators.

clusters were subsequently removed by immersing the samples in Au etchant (651818, Sigma Aldrich) for 20 seconds. The electroless metal-assisted porous etching steps were omitted for non-porous silicon resonators. Finally, silicon dioxide layers of both non-porous silicon and porous silicon resonators were removed by 49% HF solution for 2 minutes and rinsed by deionized water, followed by drying using a critical point dryer (CPD, Automegasamdri-915B) to prevent stiction.

Figure 2 shows the change of roughness from the porous etching process, which allows the porous silicon resonator to have a larger surface area than the non-porous silicon resonator of the same dimensions. It is observed that the non-porous silicon film initially has a 45 nm-deep hemispherical grain region, while the porous silicon film has nanoscale pores 110 nm into the surface.

(a)

(b)

(c)

Figure 2. A non-porous silicon resonator (left) and a porous silicon resonator (right). (a) SEM images showing $l = 15 \mu\text{m}$, $b = 5 \mu\text{m}$, and $c = d = 15 \mu\text{m}$ resonators. (b) zoomed-in SEM images of resonators in cross section. (c) AFM images. The RMS roughness of the non-porous silicon and the porous silicon are 3.8 nm and 32.9 nm , respectively.

RESULTS

Experimental setup

The frequency spectra of the resonant mass sensors were measured with a test setup that consists of a Laser Doppler Vibrometer (LDV, Polytec OFV-5000), a custom-built vacuum chamber, a microscope unit (Mitutoyo FS70) and a network analyzer (HP 8753D), as shown in Figure 3. To induce mechanical resonance, the device is mounted on a piezoelectric actuator (Thorlabs AE0203D08F) controlled by stimulus signal of the network analyzer. Measurements are performed in a vacuum chamber in order to avoid energy losses by air damping. Since the vacuum chamber has a glass viewport, observation and measurement are possible. A stainless-steel container that is connected with the vacuum chamber via a metering valve is used to control IPA (Isopropyl alcohol) vapor flow. A 633 nm He-Ne laser is used as the light source of the LDV system. Actuation of the resonator is detected by reflected light. The reflected beam is converted to an electrical signal by the LDV controller, and the network analyzer records the resonant frequency of the resonator mass sensor with a frequency resolution of 2.5 Hz .

(a)

(b)

Figure 3. (a) Schematic diagram and (b) photos of the experimental setup for mechanical actuation and readout by using a Laser Doppler Vibrometer.

Figure 4. Measured quality factor of resonators. Above 0.1 Torr , data of the non-porous silicon resonator and the porous silicon resonator are described by $Q=129/P^{0.953}$ (dashed line) and $Q=135/P^{0.823}$ (solid line), respectively. Below that pressure, intrinsic energy loss mechanism limits the quality factor.

Changes in characteristics by porosification

Air damping is frequently a dominant energy loss mechanism in sub-GHz devices that are not operated under high vacuum [11]. Since operating pressure affects air damping and is dependent on vapor concentration, it is necessary to understand the dependence of resonator quality factor on pressure. Figure 4 shows quality factor as a function of pressure for a porous silicon resonator and a non-porous silicon resonator. The quality factors of both types of resonators are strong functions of pressure down to 0.1 Torr . The quality factor dependence on pressure for the non-porous and porous silicon resonators are of the form $Q=129/P^{0.953}$ and $Q=135/P^{0.823}$, respectively. The relationship between quality factor and pressure for the simplest case has a relationship of the form $Q \propto 1/P$ [12]. Below 0.1 Torr , the quality factors are determined by damping mechanisms other than air damping. We find that the pressure range where quality factor is limited by air damping is

roughly independent of the resonators' porosity.

Resonators with a 460 nm-thick, 45 μm -long square paddle and 45 μm long, 10 μm -wide support beams have been utilized to investigate how resonant frequency and quality factor are affected when the resonators are porosified. Resonant frequency decreases as porous etch time increases due to decreased mechanical stiffness of the porous material, which is only partially offset by the reduced mass of the porous material (Figure 5 (a)). In addition, variations of the quality factor depending on porous etch condition seem to be decreased as porous etch time increases (Figure 5 (b)), although further investigation is necessary to provide any conclusions regarding the impact of porosification on quality factor.

Figure 5. Measured (a) resonant frequencies and (b) quality factors depending on etch times for porous silicon resonators. The error bars indicate the standard deviation in the data, which comprised five measurements.

Vapor detection

Figure 6 contains characteristic frequency spectra showing shifts in the torsional mode resonant frequency under 5000 ppm of IPA vapor. The resonant frequency shift is measured with respect to the partial pressure of IPA, which is normalized to one atmosphere to provide units of ppm. The porous silicon resonator displays a frequency shift significantly greater than that of the non-porous silicon resonator.

Figure 7 illustrates the different responses of the non-porous and porous silicon resonators by the change of the resonant frequency shift versus the IPA concentration during a 30 minute

Figure 6. Measured frequency spectra of (a) non-porous and (b) porous silicon resonators with no IPA (dashed line) and 5000 ppm of IPA (solid line).

Figure 7. A comparison of resonant frequency shift to gas concentration. The error bars indicate the standard deviation in the data, which consist of five measurements at five minute intervals for each concentration.

period. The porous silicon resonators show higher frequency shift ranging between 99% and 22% for different gas concentrations compared to the non-porous silicon resonators. The results demonstrate that the porous silicon-based resonators have an enhanced sensitivity to IPA vapor as compared to the non-porous silicon-based resonators.

CONCLUSION

We have demonstrated a 99% sensitivity improvement in chemical vapor sensing using porous silicon resonators. By using a microscale device with nanoscale features, we were able to leverage the best of both size scales (*i.e.*, microscale ease of fabrication with nanoscale sensitivity). Future work will focus on investigating the limits of porosity on quality factor and mechanical stability. Specifically, we will explore selectively porosifying parts of the resonators to obtain enhanced sensitivity while maintaining mechanical robustness.

ACKNOWLEDGEMENTS

The authors gratefully thank Prof. C.-J. Kim and C.Y. Lee for helping us to process the porous silicon etching. We would also like to thank Tom Lee of the Nanoelectronics Research Facility at UCLA for assistance in fabrication of the test chamber. This work was supported by the BRIGE program of the National Science Foundation under award # 0926228.

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