ZIF-COUPLED MICRORESONATOR FOR HIGHLY SENSITIVE AND SELECTIVE GAS DETECTION

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ABSTRACT

We introduce for the first time a zeolitic imidazolate framework (ZIF)-coupled resonant gas sensor whose sensitivity shows an improvement up to 78 times over silicon resonant sensors with identical dimensions while additionally utilizing the inherently selective adsorption properties of ZIFs. In order to achieve high sensitivities, a resonator needs to have a high surface-to-volume ratio. In this study, we demonstrate a microresonator coupled with ZIF crystals, which provide a level of surface area that was previously unachievable, as well as the potential for inherent selectivity.

KEYWORDS

Zeolitic imidazolate framework, resonant gas sensor, sensitivity

INTRODUCTION

ZIFs are a new class of three-dimensional crystalline structures synthesized from transition metals bridged by imidazolate. ZIFs are attracting attention for gas storage due to their ultra-high surface area, and they show promise in filtering applications due to their tailorable nanoporosity [1, 2]. These same properties of high surface area and tailorable nanoporosity (and therefore selectivity) also attractive for various sensing methodologies, such as detecting changes of impedance, refractive index and strain [3-5]. ZIF-69, one particular type of ZIF, has a high Langmuir surface area of 1070 m^2/g, enabling superior adsorption properties and a high affinity for CO_2 [6]. Previous research has investigated the potential for sensitivity enhancement with porous material coatings on resonant sensors [7]. However, this work marks the first demonstration of resonant sensors using ZIFs, which is noteworthy because ZIFs have 2.8 times more surface area than any material previously used for resonant sensing.

Resonant sensors detect chemical/biological analytes by measuring shifts in the resonance frequency due to adsorption-induced mass changes. Improved sensitivity (i.e., larger fractional frequency shifts $(\Delta f/f_0)$) typically has been achieved by miniaturization due to scaling (i.e., ratio of adsorbed mass to resonator mass), as seen in Figure 1. Ultra-small sensors, however, suffer from increased accumulation time, as longer time is required for the molecules to find the device. This problem is most extreme for detection of low concentrations (Figure 2). Rather than fabricating nanoscale devices, our approach uses highly porous ZIFs to provide both the sensitivity of nanoscale devices with the capture area of microscale devices and the selectivity to desired analytes.

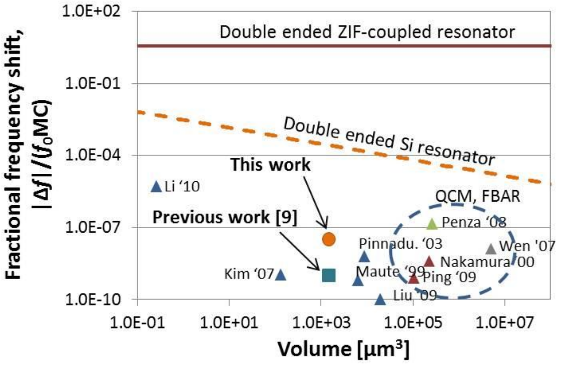

Figure 1. Frequency shift (*Δf*) from adsorbed gas normalized by product of resonant frequency (f_0), molar mass (M) and concentration (C) of gas, plotted against resonator volume. Most of the compared works (triangles) employed additional functionalized layers for enhancing sensitivity and selectivity. Points inside the dotted circle utilized QCM (quartz crystal microbalance) or FBAR (film bulk acoustic resonator) platforms. Theory predicts microscale ZIF-coupled resonators to have higher sensitivity than nanoscale silicon resonators (solid and dotted lines, assuming complete saturation of adsorption of CO_2 and an areal mass load of 28 ng/cm^2 [8]). This work achieves sensitivity improvement 32 times over the previous work using porous silicon and 78 times over the silicon resonators [9].

EXPERIMENT

As shown in Figures 3 and 4, the ZIF-coupled microresonators in this work consist of 45-µm-long, 10-µm-wide torsional beams and a 45-µm-long, 45-µm-wide center paddle. They are fabricated using sublimation drying with p-DCB (p-dichlorobenzene) and a two-step sacrificial layer process in combination with standard surface micromachining processes. ZIF-69 nanoparticles are assembled into pre-patterned target regions by a novel

978-0-9798064-5-2/µTAS 2012/$20©12CBMS-0001

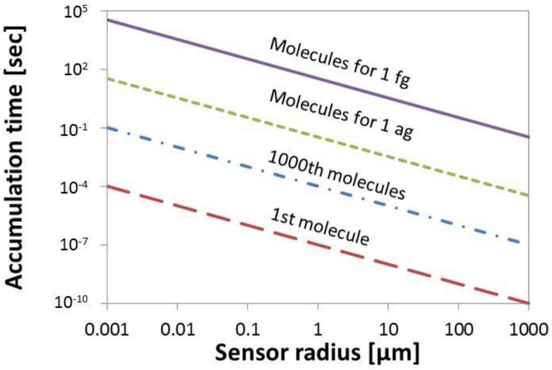

Figure 2. Required time for accumulating analyte molecules on a disk-shaped surface. H_2 gas molecules at 1 ppb are used as a model analyte for this example. For radii below 100 nm, more than 5 minutes are necessary to detect 1 fg of analytes [10].

drop-casting method, which is preferred here for its flexibility to assemble a variety of materials. The process starts with deposition of silicon dioxide (SiO_2) as the first sacrificial layer and polysilicon structural layer. After defining the resonator, the SiO_2 sacrificial layer is removed by immersing wafers in HF solution, followed by sublimation drying with p-DCB. The device is then completely underfilled and covered by PR, which is patterned using conventional photolithography techniques into a mold for ZIFs. The PR layer plays dual roles in this process, acting as both the second sacrificial layer by providing support underneath the resonator and a mold for ZIFs on top of the resonator. A dispersion of ZIFs in water is poured over the PR mold. A flat blade is used to sweep across the surface of the mold and pack the ZIFs into the trenches, ensuring agglomeration and attachment of the nanoparticles onto the center paddle of the resonator. Finally, the PR is removed with acetone to release the ZIF-coupled resonator, and sublimation drying of p-DCB is performed again to avoid stiction. The second sublimation drying procedure does not prevent the nanoparticles from providing enhanced surface area for adsorption.

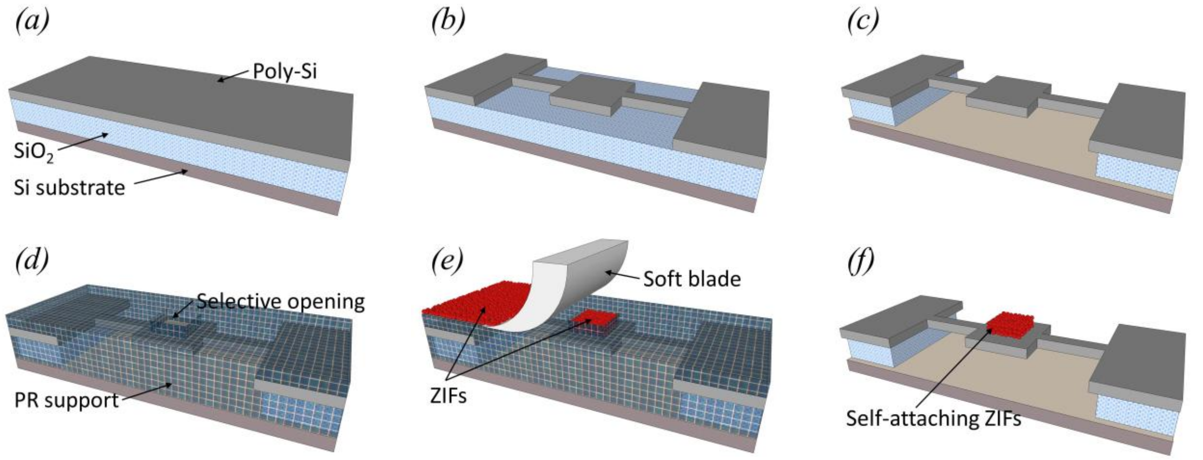

Figure 3. Fabrication process for ZIF-coupled resonator. (a) Depositing of SiO_2 and polysilicon. (b) Patterning body of the resonator via photolithography and plasma etching. (c) Etching the sacrificial layer. (d) Patterning the photoresist support structure as a sacrificial layer and cavities for a target region of ZIF particles. (e) Drop-casting ZIF particles. (f) Releasing the resonator.

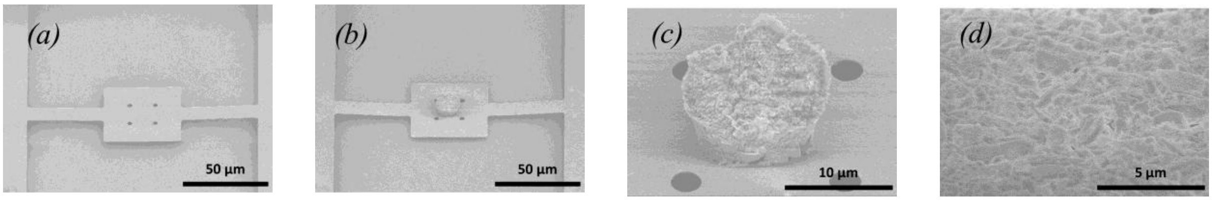

Figure 4. SEM images. (a) Polysilicon resonator without ZIF. (b) Resonator with a 10 µm × 10 µm × 3 µm casting of ZIFs. (c) Enlarged image of ZIFs attached on the surface of the resonator. (d) Raw ZIF-69 particles.

The ZIF-coupled resonators were driven by an external piezoelectric actuator and measured by an optical Doppler vibrometer. Measurements were performed in a vacuum chamber to avoid energy losses by air damping. Figure 5 shows $\Delta f/f_0$ resulting from adsorption and desorption of different gases. Figure 6 illustrates the different responses to gas of the silicon resonators with and without ZIF coupling. The ZIF-coupled resonators show higher frequency shift ranging between 35 and 78 times for different gas concentrations compared to resonators without ZIFs. Furthermore, because of the inherent selectivity of ZIFs, the ZIF-coupled resonator has 1.7 times higher sensitivity to CO_2 than IPA (isopropyl alcohol) in spite of the lighter molar mass of CO_2.

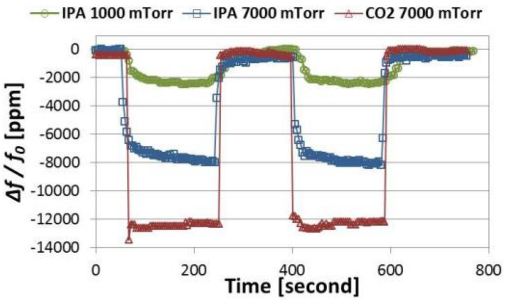

Figure 5. A typical set of real time frequency shifts exposed to IPA and CO_2 gas.

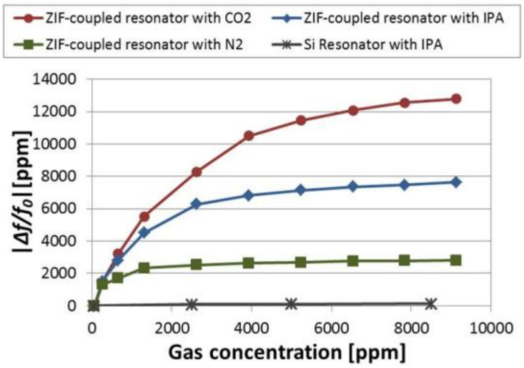

Figure 6. Response of the ZIF-coupled resonant gas sensors to N_2, IPA and CO_2 gas.

CONCLUSIONS

We have demonstrated sensitivity and selectivity improvement of chemical vapor sensing using ZIF-coupled resonators, which have ultrahigh surface area as compared to solid resonators. By using a microscale device with nanoscale features, the best of both size scales could be leveraged (i.e., microscale capture area with nanoscale sensitivity). ZIF materials hold the promise of selectivity from their material design, making them useful for a wide variety of adsorption-based sensing applications.

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