EXPLORING MICROSPHERICAL GLASS SHELL RESONATORS FOR VOLATILE ORGANIC COMPOUNDS SENSING

Jiayuan Zhang[1], Vedant Sumaria[1*], and Srinivas Tadigadapa[1]*
[1]Northeastern University, Boston, USA
*These authors contributed equally to this work.

ABSTRACT

We explore the feasibility of a volatile organic compounds (VOC) gas sensor based on an ultra-high quality-factor (Q) whispering-gallery-mode (WGM) microspherical glass (MSG) shell resonator coated with amino terminated poly(2-vinylpyridine). The change in local refractive index caused by polymer absorbing the gas molecules was monitored by the MSG resonator through a shift in its optical resonance frequency. The sensor achieved a sensitivity of 4.91 kHz/ppm to acetone and 21.44 kHz/ppm to ethanol, and the detection of down to 0.375% of ethanol is demonstrated. The limit of detection of the current sensing system is estimated to be 0.09% for ethanol and 0.4% for acetone.

KEYWORDS

Microspherical glass shell, whispering gallery mode resonator, volatile organic compounds gas sensor, microelectromechanical systems

INTRODUCTION

Detection of various volatile organic compounds (VOCs) has been increasingly of interest due to their negative health effects. More than 50 kinds of VOCs have been shown to come from various indoor sources including furniture and cleaning chemicals and have adverse health effects on humans even at low concentrations. The irritation of eye, respiratory system, headache, and nausea have been reported as the consequences of VOC exposure [1]. The ability to sense and identify VOCs at low concentrations, as a consequence, can help evaluate the indoor air quality and aid in the prevention of related health concerns. Due to their numerous applications, they have been developed on thermal, electrochemical, mechanical, and optical detection methods. Even though electrochemical sensors are the most widely used, optical sensors are an attractive alternative because they are immune to electromagnetic noise and their ability to be used in explosive medium.

Whispering gallery mode (WGM) optical resonators have been configured as highly sensitive detectors for various applications. Due to their very high *Q*-factors which results in high resolution and sensitivity, they have been configured as physical sensors such as thermal sensors, microfluidic sensors, and biosensors for the detection of bioanalytes, proteins, and bacteria. WGM resonators have been fabricated in various forms such as microring, microdisk, and microsphere [2]. Recent work has also demonstrated that wafer scale glass blowing technique can be used to form blown-glass microspherical shells configured as optical WGM resonators that can sustain ultrahigh-*Q* WGM resonances [3]. Small changes in the dimensions of the microspherical shell owing to temperature changes or surrounding refractive index or both manifest as large shifts in the resonance frequency of the WGM resonators. Polymers can be used as an absorbing medium to amplify the modification of these properties and to improve performance in the detection of gases and volatile organics.

Detection of acetone vapor realized due to the spectrum shift with refractive index change has been previously demonstrated using self-assembled PMMA-based hemispherical microlasers [4]. In this work, we fabricated microspherical shell glass resonators coated with amino terminated poly(2-vinylpyridine) and characterized the performance of these polymer-coated MSG resonators coupled to tapered optical fiber for detecting VOC vapor. When the sensor is exposed to gas vapor, polymer absorbs the gas molecules which results in a change in the local refractive index. This change results in a change of optical length of the coupled resonance, which can be monitored by the MSG resonator through a shift in its optical resonance frequency. Acetone and ethanol were chosen as the VOC vapor for sensing, and the experiment was done in two different ambient humidity levels to characterize the humidity stability of the sensor.

EXPERIMENT AND RESULTS

Sensor Fabrication

Borosilicate glass microshells are fabricated using chip-scale glass blowing process as shown in Fig. 1. A four-inch silicon wafer was patterned with 250 µm diameter circles and subsequently etched by deep reactive ion etch process to a depth of 250 µm. After etching, Remover PG® and Piranha solution were used to thoroughly clean the surface. The etched silicon wafer was then anodically bonded to a borosilicate glass wafer of 100 µm thickness, and at a positive pressure of 1000 Torr inside the bonded cavity. The bonded wafer was then diced into individual chips. A single chip was placed on a ceramic heater in a vacuum chamber maintained at a pressure of 100 Torr and was heated to 775 °C for 30 seconds, then it was gradually cooled down. During this process, the borosilicate glass was softened, and the large pressure differential created between the sealed cavities and glass blowing ambient pressure of 100 Torr formed near spherical shells.

A thin layer of polymer was then coated onto the microsphere as the gas sensitive agent. Amino terminated poly(2-vinylpyridine) was dissolved in tetrahydrofuran at 0.1 wt% concentration. The solution was placed inside a glass micropipette connected to a

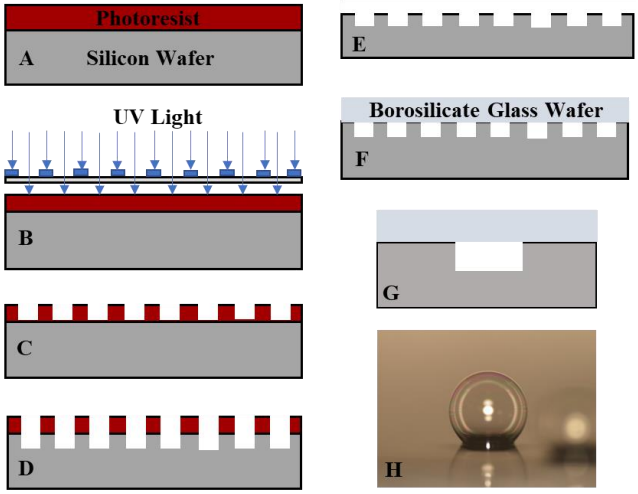

Figure 1: (a-c) Silicon wafer is patterned with circular features. (d-e) Wafer is plasma etched to a depth of 250 µm to define circular pits. (f) Borosilicate glass and the etched silicon wafers anodically bonded. (g-h) Glass microshell is blown at 775 °C in a vacuum oven maintained at a pressure of 100 Torr.

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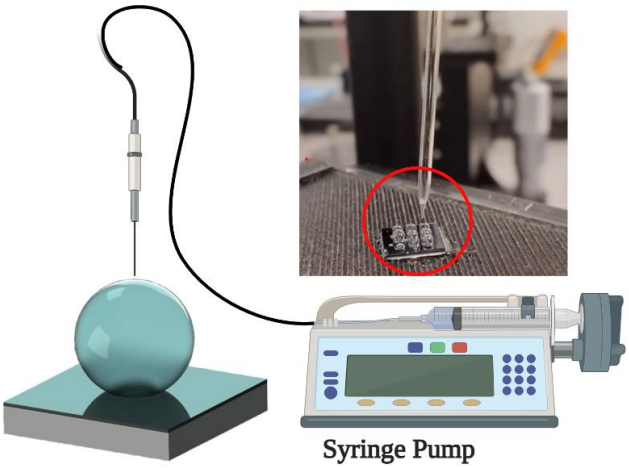

Figure 2: Amino terminated poly(2-vinylpyridine) is coated on the top half of the microspherical shell resonator using the syringe pump and micropipette. Inset: Photo of the micropipette just over the device being tested.

syringe pump as shown in Fig. 2, which drop coated the polymer solution on the outer surface of the top half of the microsphere. It was followed by a heat treatment to evaporate the solvent, leaving a thin polymer film on the surface of the microsphere.

Experimental Setup

The experimental setup for gas sensing is shown in Fig. 3. The device was placed inside a custom designed, 3D-printed testing chamber with a gas inlet. The measurement schematic for tracking the resonance frequency shift of the MSG resonator with the gas flow setup is shown in Fig. 4. Light from a tunable 1550 nm laser (Newport TLB-6728) was used as the source for the excitation of the resonance in the microspherical glass shell. The laser was tuned with a triangular wave to scan the transmission spectrum of the resonator over a 17 nm range. The laser was evanescently coupled to the microspherical glass shell resonator using a tapered optical fiber. The transmitted light intensity from the resonator was measured using a photodiode (Newport 2051-FC). The resonance curve was recorded as the sensor output signal and analyzed for shift in resonance frequency over time.

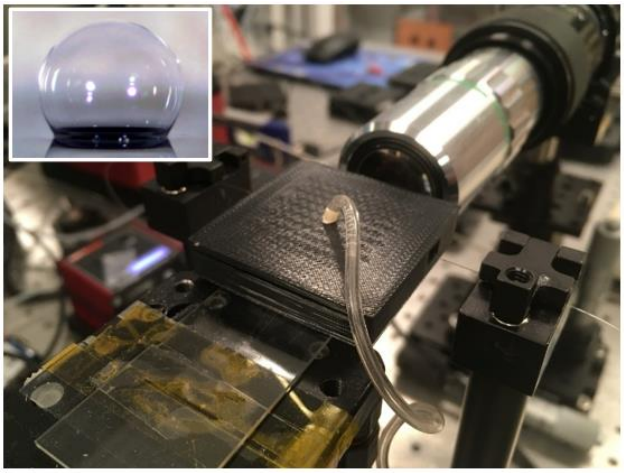

Figure 3: Experimental setup showing the MSG resonator device coupled with tapered optical fiber. The device is placed inside a 3D-printed testing chamber, with gas flowing into the chamber from the inlet. Inset: WGM microsphere before the polymer is deposited.

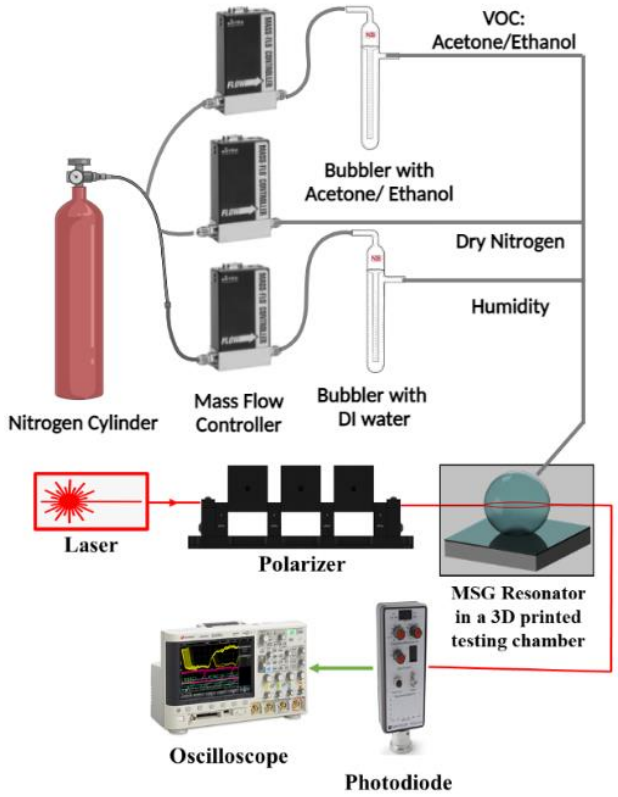

Figure 4: Schematic of the measurement system for tracing the resonance frequency shift of the MSG resonator with the control of concentration of VOC gas being detected using mass flow controller and bubblers.

The fiber tapering was performed by stripping a single mode optical fiber (SMF-28) and cleaning with acetone and isopropyl alcohol. The stripped fiber was clamped between two linear translation stages (Thorlabs MTS50-Z8) and the bare fiber section was placed into the cavity of a ceramic microheater which temperature was slowly increased to 1250 °C for the softening of the silica fiber. After reaching the thermal equilibrium, the translation stages were moved at a constant pulling rate of 40 µm/s while the transmission was monitored through the photodiode. The stages were stopped after about 20 mm of fiber stretching, the fiber was allowed to cool down to room temperature, and it was removed from the heating cavity.

The resonance in the microspherical shell occurs when the coupled light constructively interferes with itself after circulating around the circumference of the microspherical shell for an integer number of times. The condition for the WGM resonance can be describe as the following equation:

$$2\pi n_r r = m\lambda \qquad (1)$$

where r is the radius of the optical path, λ is the wavelength of the light source, n_r is the effective refractive index at the wavelength, and m is the resonance mode number. When the polymer on the microspherical shell absorbs gas molecules, its effective refractive index will be changed, and results in a change in the resonance wavelength. This spectral shift of $\Delta\lambda$ of the resonance wavelengths can be generally described as the following relation:

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta R}{R} + \frac{\Delta n}{n} \qquad (2)$$

From Eq. (2), there are two mechanisms that could contribute to the spectral shift caused by the absorption of a gas into the polymer. First is due to a change in the effective radius ΔR from polymer swelling and the second is due to the change in the refractive index Δn caused by the formation of polymer-gas blend when the gas is absorbed. Both these phenomena are linked to the concentration of the gas being detected. Among these two, the contribution of change in refractive index is much higher especially for polymers like Amino terminated poly(2-vinylpyridine) due to their high stiffness and amorphous non-crystalline structure.

The gas flowing into the test chamber was controlled by a pair of mass flow controllers which mixed specific amounts of rated VOC vapor with nitrogen to achieve multiple output concentrations of these vapors. VOC vapor used in the test was provided via nitrogen flowing through a bubbler filled with acetone or ethanol the vapor pressure of which can be determined with Antoine equation. The concentration of the vapor at the output of the bubbler under the testing conditions (1 atmosphere pressure, 25 °C temperature) was calculated to be 15% for acetone [5] and 3.75% for ethanol [6]. This vapor was then diluted by mixing with dry nitrogen to achieve the final gas concentration for acetone between 1.5% and 15%, and for ethanol between 0.375% and 3.75%. The total flow rate of the mixed gas was controlled at 200 sccm. The test was performed at two different relative humidity levels at 0% and 37%. To achieve the specific humidity level, dry nitrogen flowing through a bubbler filled with water was used as the humidity source, and the output was mixed with the diluted VOC vapor. Tests were conducted by repeated exposure and recovery of the resonator to the analyte gas, and by changing the VOC vapor concentration between zero and specific concentration points (6 distinct steps between 1.5% and 15% for acetone, and between 0.375% and 3.75% for ethanol) in 5-minute cycles. During the exposure cycles, the shift of a resonance peak was recorded in real time was calculated. The results were analyzed to determine the frequency shift of the resonators when exposed to different species and concentrations of VOC vapors. The same test was also conducted with a microspherical shell resonator without any polymer coating as a reference. The idle state of the resonator was recorded to determine the noise level of resonance frequency.

Results & Discussion

Fig. 5 shows the typical WGM resonance curve of the MSG resonator. The resonance frequency of the resonator was 193.5 THz, corresponding to a wavelength of 1550 nm. After the deposition of the polymer on the microspherical shell, the resonator showed a Q-factor of 827,618, a factor of 10 times reduction from the pristine state in the range of 8.1 million. This reduction is because of increased scattering loss due to the polymer deposition on the surface of the microspherical shell.

Fig. 6 shows the resonance frequency shift during gas testing cycle for acetone vapor exposure at 0% humidity, correlating to the increasing acetone vapor concentrations flowing into the test chamber. The sensor showed an increased frequency shift with increasing VOC vapor concentration. A response time constant of about 100 seconds was experimentally measured for a change in vapor concentration. The calculated time constant could be larger than that of the devices themselves because it includes the time needed for the testing chamber to reach the equilibrium state at gas concentration. The reference resonator without the polymer coating did not show any observable frequency shift during testing, suggesting that the change of refractive index of polymer coating plays an essential role for the detection of the VOC vapors.

The frequency shift was extracted from the frequency-time data and represented as a function of VOC vapor concentration for

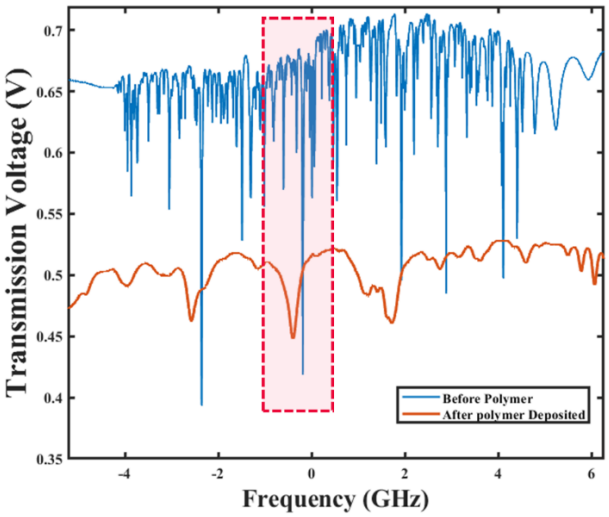

Figure 5: Typical transmission spectrum of the microspherical shell glass resonator used here to perform the gas sensing. Blue: Typical resonance curve of the device with Q-factor in the range of 8.1 million. Red: Resonance curve after polymer is deposited with Q factor of 827,618.

acetone and ethanol under two different humidity levels. The plotted data is shown in Fig. 7. The relationship between VOC vapor concentration and the resonance frequency shift showed a linear dependence in a wide range of concentration for both acetone and ethanol VOC vapors, and at both humidity levels tested. The data points were linear fitted and the sensitivity of the resonator was determined. The result is shown in Table 1. The sensor showed a high sensitivity of 4.91 kHz/ppm to acetone and 21.44 kHz/ppm to ethanol and exhibited about 4 times greater sensitivity to ethanol against acetone, with the selectivity behaving consistently under the two humidity levels under which the tests were performed. A small increase in sensitivity at 37% humidity was observed. This could imply that the presence of water at 37% RH caused the polymer to exhibit a larger refractive index change during the gas exposure compared to dry environment. The noise of the sensor is calculated from its idle state to be 20 MHz, resulting in the limit of detection of 0.09% for ethanol and 0.4% for acetone. The limit of detection is

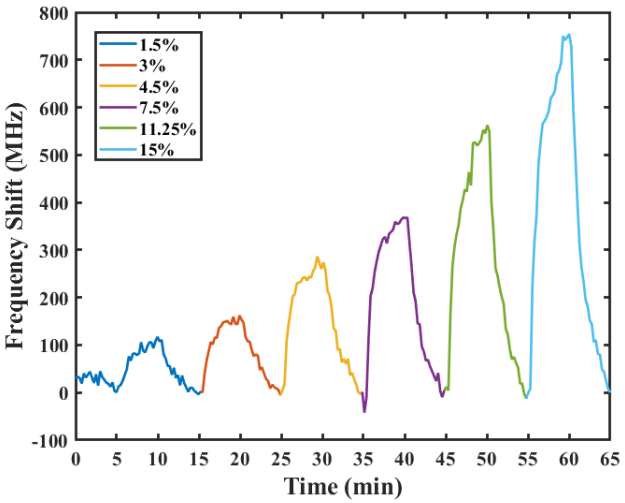

Figure 6: Resonance frequency shift during the acetone vapor exposure at 0% humidity. The concentration of the acetone vapor in this test is varied from 1.5% to 15%.

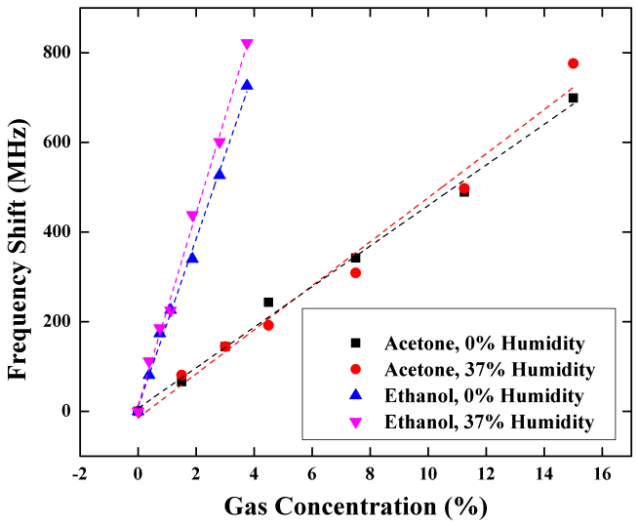

Figure 7: Resonance frequency shift as a function of VOC vapor concentration exposed to the MSG resonator at different relative humidity levels. Dashed lines show linear fit.

Table 1: Sensitivity of the resonator to acetone and ethanol under 0% and 37% humidity levels.

Sensitivity (kHz/ppm)	Acetone	Ethanol
0% Humidity	4.53	18.77
37% Humidity	4.91	21.44

currently limited by the reduced *Q*-factor after polymer coating, which can be improved by developing improved printing methods to reduce scattering loss, and by using the PID controller method for frequency locking. Previous work where similar sensor is used for IR sensing mentions the use of Pound-Drever-Hall (PDH) adaptive locking of the laser frequency at a fixed point on the slope of the resonance curve [7]. The laser was used in combination with a DigiLock 110 from Toptica Photonics. The output of the photodetector was connected to a feedback proportional-integral-derivative (PID) controller, which in turn tunes the voltage-controlled laser frequency and keeps it locked at the same point on the shifted resonance curve upon any physical change to the device. This would significantly reduce the noise arising from random fluctuations in the resonance frequency and thereby significantly improve the signal to noise ratio (SNR).

CONCLUSIONS

We have explored the feasibility of a volatile organic compounds (VOC) gas sensor using an ultrahigh-*Q* whispering gallery mode microspherical glass shell resonator coated with polymer. The change in local refractive index caused by polymer absorbing the gas molecules results in an optical resonance frequency shift in the sensor. The sensor achieved a sensitivity of 4.91 kHz/ppm to acetone and 21.44 kHz/ppm to ethanol, a time constant of 100 seconds, and demonstrated the detection down to 1.5% for acetone and 0.375% for ethanol. The selectivity between ethanol and acetone was observed to be preserved at the two tested humidity levels. The current sensing system achieved a limit of detection of 0.09% for ethanol and 0.4% for acetone. With tailored polymer selection, improved *Q*-factor after the polymer coating, and better testing set-up, polymer-coated whispering gallery mode microspherical shell glass resonators present a huge promise for being used as a general VOC gas sensing platform.

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CONTACT

*Jiayuan Zhang, zhang.jiayu@northeastern.edu