ON-CHIP OPTOFLUIDIC RING RESONATOR SENSOR FOR MICRO-SCALE GAS CHROMATOGRAPHY

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ABSTRACT

The design, fabrication and preliminary performance assessment of a new vapor sensor comprising a *microfabricated* optofluidic ring resonator (μ OFRR) and its application to micro-scale gas chromatographic (μ GC) detection of volatile organic compounds (VOC) are presented. The μ OFRR combines vapor sensing and fluidic transport functions in a micro-fabricated whispering gallery mode (WGM) resonator. The device also integrates on-chip fluidic-interconnection and fiber-optic probe alignment features. We demonstrate sub-second, sub-ng VOC detection and also couple the μ OFRR to an upstream μ GC column for rapid analysis of a simple VOC mixture.

INTRODUCTION

Advances in photonics have yielded a new class of (bio)chemical sensors adapted from WGM resonators [1], wherein shifts in resonant frequencies (λ_{WGM}) reflect analyte interactions with a sensitive interface layer. The optofluidic ring resonator (OFRR) merges sensing and fluidic transport into a single structure [2]: the evanescent components of WGMs, excited in the wall of a dielectric capillary by an external waveguide, extend into the interior of the OFRR, and changes in RI at the inner surface can cause a shift in λ_{WGM} . Previous iterations include heat-drawn glass capillaries with sorptive-polymer films [3,4], and self-rolled microtubes of semiconductor multi-layers [5]. Yet, devices reported to date have not had the small size, durability, precision fabrication, high Q-factors, and fluidic compatibility for integration into μ GC systems suitable for multi-VOC analyses in environmental or clinical applications.

Here we unveil a 1st-generation μ OFRR vapor sensor that improves upon prior OFRR designs and performs as well as, or better than, other microsensors used as GC/ μ GC detectors [6-8]. Our device integrates a PDMS-coated, SiO_x μ OFRR cylinder (250- μm i.d., 1.2- μm wall; 85- μm tall), a microfluidic interconnection channel, capillary insertion port, and an optical-fiber alignment structure on a 2 $\times$ 2-cm Si chip (Fig. 1). High-Q ($> 10^4$) WGM resonances are excited in a centrally located quasi-toroidal mode-confinement expansion in the μ OFRR by a 1550-nm laser via a fiber waveguide. This is a refinement of μ OFRR test structures we have made [9], which lacked a complete fluidic pathway.

EXPERIMENTAL

μ OFRR Fabrication

The μ OFRR sensor was micromachined from Si. The resonator cylinder pre-form was made by through-wafer DRIE. An interim isotropic XeF_2 etch created a quasi-toroidal midsection expansion for mode confinement. Sidewalls were oxidized and HF-etched to reduce surface roughness before a final thermal oxidation step created the SiO_x μ OFRR. The resonator was then partially released with a XeF_2 etch to a height of 85 μm .

Backside DRIE was used to create a tapered trench for capillary insertion, and a microfluidic channel connecting the capillary port and backside μ OFRR aperture. A final frontside DRIE step created an optical-fiber alignment channel running laterally across the surface. Devices were diced into 2 $\times$ 2 cm chips.

An internal PDMS layer was deposited in the μ OFRR by filling the resonator cavity with a toluene solution of PDMS and evaporating the solvent. The backside fluidic channels were sealed with a 2 $\times$ 2 cm Pyrex coverplate using UV curable glue. A short section of fused-silica capillary (250 μm i.d.) was sealed into the completed device for external fluidic connection.

Fig. 1: a, Concept drawing of the μ OFRR sensor configuration. b, SEM of μ OFRR with tapered optical fiber (right) in contact with the quasi-toroidal expansion. c, Photo of the μ OFRR sensor chip.

μ OFRR Sensor Tests

WGM resonances were excited in the μ OFRR wall by evanescently coupling a laser signal from a thinned optical fiber (~ 1 μm o.d.), placed in contact with the μ OFRR expansion. The fiber was connected to a tunable 1550 nm laser source and an IR photoreceiver. The laser wavelength was swept over a 375 pm range at 10 Hz while the transmitted signal was recorded.

The WGM was evident as a Lorentzian trough in the transmitted intensity. λ_{WGM} was defined as wavelength of minimum transmission and sensor response was defined as a shift in λ_{WGM} due to VOC exposure. Test atmospheres of benzene, toluene,

ethylbenzene, m-xylene, and n-octane were created in Tedlar bags at 5 concentrations. VOC aliquots were collected in a 1-mL sample loop and injected into the μ OFRR in dry air at 3 mL/min. This was repeated with m-xylene using a 5- μ L sample loop to evaluate responses to transient exposures.

For μ GC integration tests, the μ OFRR was connected downstream from a 3 $\times$ 3cm chip containing a 3-m long PDMS-coated DRIE separation μ column. A 4-VOC mixture was injected (5- μ L loop) into the μ column in dry air at 1.4 mL/min.

RESULTS AND DISCUSSIONS

All VOC exposures induced reversible red shifts in λ_{WGM} , with rapid steady-state responses for all VOCs (rise and fall times < 2.5 s and < 5.8 s, respectively). Fig. 2 presents calibration curves for the five individual vapors from steady-state responses. Sensitivity was defined as the slope of the calib. curve in pm/(mg/m³), and limit of detection (LOD) was defined as $3\sigma/\text{sensitivity}$, where σ is the std. deviation of the baseline. LODs ranged from 2.2 (benzene) to 22 mg/m³ (ethylbenzene). The high sensitivity is attributed, in part, to the thin walls of the μ OFRR, which increase the portion of the WGM probing the polymer film.

Fig. 2: Calibration curves for benzene (diamond), toluene (square), ethylbenzene (triangle), m-xylene (filled circle), and n-octane (unfilled circle) vapors. Inset shows the response profile to 700 mg/m³ of toluene, while red square shows < 2.5 s rise time.

For transient exposures, peak height and peak area varied linearly ($R^2 > 0.997$) with injected mass. The calculated LOD of 49 pg is 10-1,000 $\times$ lower than those of other microsensors adapted as μ GC detectors [6,7] and $\sim 100\times$ lower than a polymer-coated capillary-based OFRR [4]. Fig. 3 shows the μ OFRR response profile for 180-pg injection of m-xylene (FWHM = 0.71 s) compared to a similar injection for a commercial FID under the same conditions (FWHM = 0.60 s). This demonstrates the very low effective dead volume of the μ OFRR which, combined with its rapid response time, is critical for a high-speed μ GC detector.

Fig. 4 shows the separation/detection of four VOCs with a μ GC column chip coupled to the μ OFRR sensor. VOCs are easily separated in < 40 s and peaks are symmetric and sharp (FWHM = 0.33-1.17 s), reflecting excellent sensor response dynamics.

CONCLUSIONS

This is the first report of a microfabricated OFRR sensor and the first report of an on-chip optofluidic resonator for VOC sensing. Sensitivity is outstanding and response time is sufficient to capture very narrow peaks containing sub-ng quantities of vapor. This design reduces the size, increases structural integrity, and grants precise control of resonator dimensions, allowing for thinner walls and increased sensitivity, when compared to capillary drawn OFRRs. This is also the first report of an optofluidic resonator used to together with a μ GC column. Results augur well for integration of the μ OFRRs into μ GC systems.

Fig. 3: Response profiles from the μ OFRR (solid black line, left axis) for a 180-pg injection of m-xylene and the FID (dashed green line, right axis) for a ~ 500 -pg injection of m-xylene; scaling of y axes facilitate comparison of full-width-at-half-maximum (FWHM).

Fig. 4: Separation of benzene, toluene, n-octane and m-xylene using a μ column chip containing a 3-m long PDMS-coated channel at 63 °C and the (downstream) μ OFRR sensor at 22 °C.

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