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 (μOFRR) and its application to micro-scale gas chromatographic (μGC) detection of volatile organic compounds (VOC) are presented. The μOFRR combines vapor sensing and fluidic transport functions in a microfabricated 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 integrates on-chip fluidic-inte rconnection and fiber-optic probe 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 μOFRR to an upstream μGC 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 (λWGM) 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 λWGM. 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 μGC systems suitable for multi-VOC analyses in environmental or clinical applications.

Here we unveil a 1st-generation μOFRR vapor sensor that improves upon prior OFRR designs and performs as well as, or better than, other microsensors used as GC/μGC detectors [6-8]. Our device integrates a PDMS-coated, SiO, μOFRR 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 2×2-cm Si chip (Fig. 1). High-Q (> 106) WGM resonances are excited in a centrally located quasi-toroidal mode-confinement expansion in the μOFRR by a 1550-nm laser via a fiber waveguide. This is a refinement of μOFRR test structures we have made [9], which lacked a complete fluidic pathway.

EXPERIMENTAL
μOFRR Fabrication
The μOFRR sensor was micromachined from Si. The resonator cylinder pre-form was made by through-wafer DRIE. An interim isotropic XeF2 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, μOFRR. The resonator was then partially released with a XeF2 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 μOFRR aperture. A final frontside DRIE step created an optical-fiber alignment channel running laterally across the surface. Devices were diced into 2×2 cm chips.

An internal PDMS layer was deposited in the μOFRR by filling the resonator cavity with a toluene solution of PDMS and evaporating the solvent. The backside fluidic channels were sealed with a 2×2 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.

μOFRR Sensor Tests
WGM resonances were excited in the μOFRR wall by evanescently coupling a laser signal from a thinned optical fiber (~1 μm o.d.), placed in contact with the μOFRR expansion. The fiber was connected to a tunable 1550 nm laser source and an IR photoreciever. 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. λWGM was defined as wavelength of minimum transmission and sensor response was defined as a shift in λWGM 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 µOFRR in dry air at 3 mL/min. This was repeated with m-xylene using a 5-µL sample loop to evaluate responses to transient exposures.

For µGC integration tests, the µOFRR was connected downstream from a 3×3cm chip containing a 3-m long PDMS-coated DRIE separation µcolumn. A 4-VOC mixture was injected (5-µL loop) into the µcolumn in dry air at 1.4 mL/min.

RESULTS AND DISCUSSIONS

All VOC exposures induced reversible red shifts in \( \lambda_{WGM} \), 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 calibration curve in pm/(mg/m³), and limit of detection (LOD) was defined as 3σ/sensitivity, where σ is the standard 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 µOFRR, which increase the portion of the WGM probing the polymer film.

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× lower than those of other microsensors adapted as µGC detectors \([6,7]\) and ~100× lower than a polymer-coated capillary-based OFFR \([4]\). Fig. 3 shows the µOFRR 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 µOFRR, which, combined with its rapid response time, is critical for a high-speed µGC detector.

Fig. 4 shows the separation/detection of four VOCs with a µGC column chip coupled to the µOFRR 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 µGC column. Results augur well for integration of the µOFRRs into µGC systems.