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Waveguide-Enhanced Raman Spectroscopy Using a Mesoporous Silica Sorbent Layer for Volatile Organic Compound (VOC) Sensing

Haolan Zhao[1,2*], Ali Raza[1,2], Bettina Baumgartner[3], Stéphane Clemmen[1,2], Bernhard Lendl[3], Andre Skirtach[2,4], Roel Baets[1,2]

[1] *Photonics Research Group, Ghent University-IMEC, 9052 Ghent, Belgium*
[2] *Center for Nano- and Biophotonics, Ghent University, 9052 Ghent, Belgium*
[3] *Institute of Chemical Technologies and Analytics, Technische Universität Wien, 1060 Vienna, Austria*
[4] *Department of Biotechnology, Ghent University, 9000 Ghent, Belgium*
Author e-mail address: haolan.zhao@ugent.be

Abstract: We report a Raman sensor for broadband vapor-phase volatile organic compounds (VOCs) based on SiN waveguides functionalized with a mesoporous silica top-cladding. A detection limit below 1000ppm is demonstrated and scaling to trace-gas-levels is discussed.

OCIS codes: (300.6450) Spectroscopy, Raman; (130.6010) Sensors; (230.7370) Waveguides

Volatile organic compounds (VOCs) are organic chemicals with a high vapor pressure at room temperature. VOCs include some components, such as formaldehyde, benzene, toluene, and xylenes, that represent a risk factor to human health [1]. Driven by the increasing awareness of environmental protection and personal safety, rapid detection of VOCs in the indoor/outdoor environment with low cost has been a major focus of sensor research in recent years. The challenge is to detect VOCs at low concentration from a complex atmospheric ambient, which demands methods with high sensitivity and high specificity.

Raman spectroscopy is a promising candidate for VOC detection due to its ability to identify simultaneously all the components in a sample over a wide range of concentration. However, the extreme weakness of the Raman scattering process has limited its applicability in low-concentration gas analysis. One approach to enhance the Raman signal is to tightly confine both the optical excitation and the analyte within an optical waveguide [2]. In this way, the Raman signal is significantly intensified through an increased interaction volume. The silicon nitride (SiN) waveguide platform is well-established for this waveguide-enhanced Raman spectroscopic (WERS) technique. On the one hand, silicon nitride has a relatively high refractive index that is favorable for the waveguide enhancement. On the other hand, the silicon nitride platform is well-established in a CMOS-fab environment. In the past years, SiN WERS has already been employed to detect bulk liquid of isopropyl alcohol (IPA) [2] and biological monolayers [3]. Recently, gases in trace concentration have also been probed by hypersorbent polymer functionalized waveguides [4, 5]. However, the sorbent layer in these works is a specially designed polymer that bonds selectively with organophosphates and other toxics, and its application to VOCs is limited.

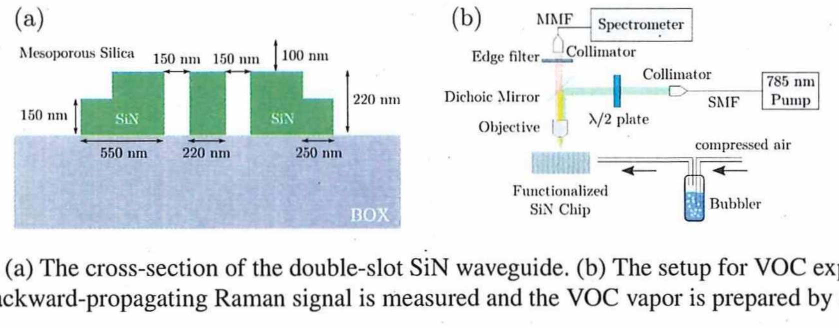

Fig. 1. (a) The cross-section of the double-slot SiN waveguide. (b) The setup for VOC experiments. The backward-propagating Raman signal is measured and the VOC vapor is prepared by a bubbler.

In this work, we report the proof-of-concept demonstration of VOC sensing using a double-slot SiN waveguide functionalized with a mesoporous silica top-cladding. The cross-section of the waveguide structure is shown in Fig. 1(a). The waveguides are comprised of a 220-nm-thick layer of silicon nitride deposited through Plasma-Enhanced Chemical Vapor Deposition (PECVD) on 3-µm thick of silica. The waveguide is patterned via deep-UV lithography and reactive ion etching (RIE) at IMEC. The waveguide has two slots and winged tails, with the aim to reduce the waveguide loss at a minimal sacrifice of Raman gain. A 100-nm-thick sorbent layer is then deposited on top of the waveguide. This high-internal-surface material is known for its high adsorption capacities for a broad range of VOCs [6]. The modal overlap for the fundamental quasi-TE mode with the sorbent layer is estimated to be 32 % at 785 nm. The length of the waveguide is 0.55 cm. We have used a confocal Raman microscope (Witec Alpha 300 R) with a 785 nm pump laser for our measurement as shown in Fig. 1(b). The polarization of the pump beam is controlled to excite the fundamental quasi-TE mode. The pump power before the objective is measured to be 44 mW. We used the backward-propagating configuration. The same objective (40X, NA=0.6) is used to couple-in the pump beam and couple-out the Stokes Raman signal. The latter is sent to a spectrometer (equipped with Andor iDus 401 camera) for analysis. The integration time of all the measurements is 0.05 s.

We first record the Raman background of the functionalized waveguide by sending only air onto the waveguide. The result is shown as the blue dashed curve in Fig. 2(a). Then, pure IPA liquid is added into the bubbler, introducing saturated IPA vapor into the air flow. The Raman spectra after the introduction of IPA vapor is shown as the orange solid line in Fig. 2(a). We can readily observe not only the intense Raman peak at 819 cm^{-1} corresponding to the in-phase C-C-O stretch vibration of IPA, but also the resonance modes at 953 cm^{-1}, 1134 cm^{-1} and 1453 cm^{-1}. The position and relative intensity of these modes are in good agreement with the reference Raman spectra of liquid IPA measured with the same Raman microscope, shown as the black dotted line in Fig. 2(a).

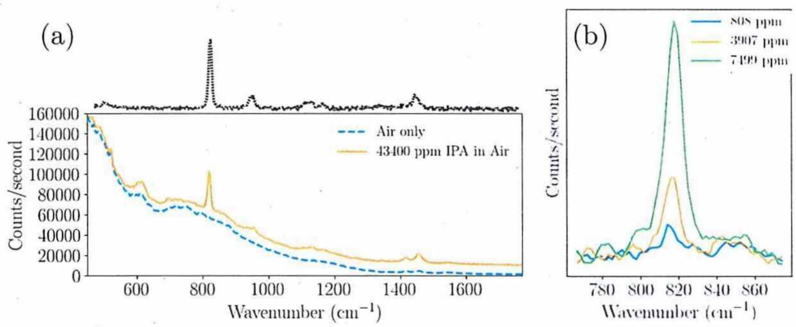

Fig. 2. (a) The Raman spectra before (blue dashed line) and after (orange solid line) the application of saturated IPA vapor. Reference Raman spectra from pure liquid IPA is also given (black dotted). (b) The background-subtracted Raman spectra of the 819 cm^{-1} mode at various concentrations.

To investigate the sensitivity of our functionalized waveguide, we reduced the concentration of IPA vapor in the air flow by diluting IPA liquid with water in the bubbler, and the exact vapor concentration is estimated by Raoults law. Fig. 2(b) shows the background-subtracted Raman spectra of the 819 cm^{-1} mode at various concentrations. It is clear that our sample is at least capable of probing IPA vapor with a concentration of as low as 808 ppm. The mesoporous sorbent layer has also been tested with other VOCs, including ethanol and toluene, showing its capability of broadband VOC sensing. A temporal analysis shows that the response time of the functionalized waveguide to VOCs is in the range of 1 s, confirming the reversibility of the ad- and de-sorption process. It suggests that our waveguide can be used for real-time VOC monitoring.

The current operation conditions have not reached the ultimate performance of the functionalized waveguide yet. Currently, the integration time of the spectrometer is limited to avoid saturating the spectrometer by the Raman background. An optimized waveguide design can suppress the background and allow for a longer integration time. We also note that the waveguide is too short to maximize the backward-propagating signal. By implementing these improvements, we expect to probe VOCs at the level of 10 ppm ppm with a 100-s integration time.

To conclude, we have demonstrated VOC sensing on a functionalized silicon nitride waveguide. This demonstration leverages both waveguide enhancement and chemical adsorption, and IPA at a relatively low concentration is probed. We believe this work constitutes a significant step forward towards an all-on-a-chip Raman sensor suitable for environmental monitoring and clinical diagnosis.

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Executive Ballroom 210E

Executive Ballroom 210F

Executive Ballroom 210G

Executive Ballroom 210H

CLEO: Science & Innovations

STh1E • Mid-IR Lasers—Continued

STh1E.7 • 09:30
Mid-IR Optical Refrigeration: Optical Cryocoolers and Radiation Balanced Lasers, Saeid Rostami[1], Azzurra Volpi[1], Alexander R. Albrecht[1], Mauro Tonelli[2], Mansoor Sheik-Bahae[1]; [1]*Univ. of New Mexico, USA;* [2]*NEST-CNR, Dipartimento di Fisica, Universita' di Pisa, Italy.* Optical refrigeration in Tm- and Ho-doped crystals is investigated, and their external quantum efficiency, background absorption, and minimum achievable temperatures are reported. Potential of these crystals for mid-IR cryocoolers and radiation balanced lasers are discussed.

STh1F • Chip-Scale Trace-Gas Sensing—Continued

STh1F.6 • 09:30
Suspended Membrane InGaAs Photonic Crystal Waveguides for ammonia sensing at Lambda=6.15um., Kyoung Min Yoo[1], Jason Midkiff[1], Ali Roastamian[1], Swapnajit Chakravarty[2], Ray T. Chen[1,2]; [1]*Electrical and Computer Engineering, The Univ. of Texas at Austin, USA;* [2]*Omega Optics Inc., USA.* Fully suspended InGaAs waveguide devices with holey photonic crystal waveguides (HPCWs) are designed for mid-infrared sensing at labmda=6.15um in the low index contrast InGaAs-InP platform. We experimentally detect 5ppm ammonia in 1mm long suspended HPCWs.

STh1F.7 • 09:45
Waveguide-Enhanced Raman Spectroscopy Using a Mesoporous Silica Sorbent Layer for Volatile Organic Compound (VOC) Sensing, Haolan Zhao[1,2], Ali Raza[1,2], Bettina Baumgartner[3], Stephane Clemmen[1,2], Bernhard Lendl[3], Andre Skirtach[4], Roel Baets[1,2]; [1]*Photonics Research Group, INTEC, Gent Univ., Belgium;* [2]*Center for Nano- and Biophotonics, Ghent Univ., Belgium;* [3]*Inst. of Chemical Technologies and Analytics, Technische Universität Wien, Austria;* [4]*Dept. of Molecular Biotechnology, Ghent Univ., Belgium.* We report a Raman sensor for broadband vapor-phase volatile organic compounds (VOCs) based on SiN waveguides functionalized with a mesoporous silica top-cladding. A detection limit below 1000ppm is demonstrated and scaling to trace-gas-levels is discussed.

STh1G • Frequency Comb Spectroscopy—Continued

STh1G.6 • 09:30
Singular spectrum analysis for low SNR signal processing in dual-comb distance measurements, Hui Cao[1], Youjian Song[1], Runmin Li[1], Yuepeng Li[1], Ming-lie Hu[1], Chingyue Wang[1]; [1]*Tianjin Univ., China.* We utilize singular spectrum analysis based post-processing approach to reduce distance measurement uncertainty for moving targets in dual-comb absolute ranging.

STh1G.7 • 09:45
Nanophotonic supercontinuum based mid-infrared dual-comb spectroscopy, Hairun Guo[1], Wenle Weng[1], Junqiu Liu[1], Fan Yang[2], Wolfgang Hänsel[3], Camille-Sophie Bres[4], Luc Thévenaz[2], Ronald Holzwarth[3], Tobias J. Kippenberg[1]; [1]*LPQM, École Polytechnique Fédérale de Lausanne, Switzerland;* [2]*GFO, École Polytechnique Fédérale de Lausanne, Switzerland;* [3]*Menlo Systems GmbH, Germany;* [4]*PHOSL, École Polytechnique Fédérale de Lausanne, Switzerland.* We demonstrate a broadband mid-infrared dual-comb spectroscopy for parallel gas-phase detection in the functional group region from 2800—3600cm^{-1}, using dispersion engineered silicon nitride dual-core waveguides which produce broadband, intensity-enhanced and coherent mid-infrared frequency combs.

STh1H • Optical Resonance-Based Devices—Continued

STh1H.6 • 09:30
Fabry-Perot Cavity Using Two Row Photonic Crystal in a Multimode Waveguide, Manuel Mendez-Astudillo[1], Hideaki Okayama[2], Tomohiro Kita[1]; [1]*Waseda Univ., Japan;* [2]*Research & Development Center, Oki Electric Industry Co., Ltd, Japan.* We experimentally present a Fabry-Perot cavity that uses two-row photonic crystals in a multimode waveguide as the reflecting elements in an add-drop configuration to achieve fine FSR tuning and maximum footprint efficiency.

STh1H.7 • 09:45
New Resonance Behavior based on Bound States in the Continuum in a Silicon Photonic Waveguide Platform, Thach Nguyen[1], Guanghui Ren[1], Steffen Schoenhardt[1], Markus Knoerzer[1], Andreas Boes[1], Arnan Mitchell[1]; [1]*School of Engineering, RMIT Univ., Australia.* A new type of resonance in silicon photonics is demonstrated, achieved by coupling between a continuum of TE slab modes to a discrete TM mode of a silicon ridge to create a single sharp resonance.

10:00–11:30 Exhibit Open (10:00–15:00), Coffee Break (10:00–11:30), *Exhibit Halls 1–3*
Coffee Break Sponsored by COHERENT and THORLABS

10:15–12:00 Technology Transfer Program, *Exhibit Hall Theater I*
