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Photonic Integrated Circuit Assisted Photothermal Spectroscopy

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***Abstract*—For the first time, we demonstrate on-chip photothermal spectroscopy of a liquid phase sample, namely water in isopropanol and will show how this technique can be used to realize compact highly sensitive and selective sensors for a range of analytes.**

Keywords—photothermal spectroscopy, silicon nitride, refractive index sensing, micro ring resonator, optical sensing

I. INTRODUCTION

Photonic sensors based on Laser Absorption Spectroscopy (LAS) are of growing interest for process monitoring, environmental monitoring, medicine amongst others, particularly due to the recent development of powerful mid-infrared lasers tunable over large wavelength ranges. These permit unambiguous detection of numerous substances at low concentration, often with calibration free operation. They are considerably faster than established analyzers (e.g. wet-chemical or chromatographic systems) and significantly more reliable than non-photonic approaches (such as electrochemical or mass sensitive transduction).

Nonetheless, mid IR spectroscopy systems are complex, delicate and expensive, which limits their potential for deployment. Furthermore, the target molecules often show weak absorption and to reach the required sensitivities either long pathlengths or an optical build up cavity, consisting of two or more precisely aligned highly reflective mirrors, is often employed to increase the optical path length in the system, resulting in spectroscopy systems that are either very delicate or expensive.

Photoacoustic spectroscopy is a family of spectroscopic techniques in which the modulated absorption of light by materials leads to modulated heating of the sample causes a thermal expansion that generates acoustic and thermal waves. The magnitude of the measured signal is directly proportional to the induced pressure/temperature change and thus to the concentration of the sample in contrast to laser absorption spectroscopy which is based on the Beer-Lambert absorption law. Furthermore, the generated signal is directly proportional to the intensity (laser power divided by the laser beam cross section) at the place of sample excitation. Thus, there is a synergy between Photothermal spectroscopy (PTS) and integrated photonics that creates potential for the creation of low cost, compact, high performance spectroscopy systems [1].

In this work, we demonstrate a photothermal sensor that uses a silicon nitride micro-ring resonator (MRR) refractive index sensor as a transducer, with a mid-infrared external cavity quantum cascade laser (EC-QCL) as the excitation source for a PTS measurement of water in ethanol as a proof-of-concept, shown schematically in figure 1.

We use a tunable near-infrared (NIR) laser set to the inflection point of a resonance of the MRR to maximize the wavelength shift sensitivity. The EC-QCL that emits between 1560-1770 cm^{-1} (6410.26-5649.72 nm), covering the spectral region in which water in isopropanol has a strong absorption band. While the water in isopropanol measurement was selected as a proof of principle, such a measurement has potential as a reagent free alternative to the "Karl-Fischer titration" method, which is the standard technology for measuring trace water content in organic liquids but which can only be applied off-line, consuming sample and generating waste. Photonic Integrated Circuit (PIC) assisted Photothermal Spectroscopy can be applied to a wide range of analytes in both the liquid and gas phases e.g. proteins and and methane and environmental pollutants respectively.

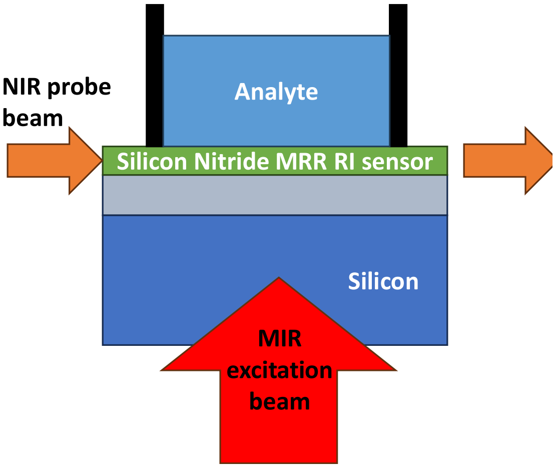

Figure 1. Schematic of the Photothermal spectroscopy measurement with the silicon nitride micro-ring resonator providing a sensitive transducer.

II. BACKGROUND

The basic principle behind photothermal spectroscopy dates back to Alexander Graham Bell who discovered that modulated absorption of light by materials leads to modulated heating of the sample generating acoustic and thermal waves. Since 2000, advances in performance of interband and quantum cascade lasers have accelerated the growth of this field and made these techniques very popular. In a recent evolution of PTS [2], a Fabry-Perot (FP) interferometer has been used as a sensitive transducer for detection of induced refractive index changes in the gas sample. The excitation laser beam is tuned to an absorption line of the target analyte and intensity modulated. The periodic excitation of the analyte molecules inside the FP etalon through absorption of laser radiation leads to a periodic modulation of the gas temperature due to photothermal heating, which causes a change of the refractive index and the etalon transmission function is shifted. The etalon acts as a transducer, providing a signal when the target gas absorbs.

The photoinduced temperature change ΔT is given by the following equation, which highlights the attractiveness of miniaturization as the signal scales with the laser power and inversely with the volume of the beam that interacts with the sample V[3].

$$\text{Signal} \propto \Delta T \propto \frac{P(\tilde{\nu})\,\alpha(\tilde{\nu})\,L}{\rho C_P V f_{mod}} \qquad (1)$$

Where the laser power is $P(\tilde{\nu})$, the analyte linear absorption coefficient $\alpha(\tilde{\nu})$, the optical pathlength L, the applied modulation frequency f_{mod}

III. MEASUREMENTS

MRRs were fabricated using thermally oxidized Silicon wafers (BOx thickness of 2.2 µm) with a SiN layer (300 nm thick), deposited with plasma enhanced chemical vapor deposition (PECVD). The devices layouts were patterned electron beam lithography (EBL) using 100 kV voltage transferred to the SiN layer through inductively coupled plasma (ICP), see Figure 2. The analyte (isopropanol with different dilutions of water was contained in the rubber tube positioned on the MRR.

To perform the PTS experiment, we illuminated the chip and analyte from below, (See figure 1) by means of a Cassegrain reflector. The reflective microscope objective ensured the minimum beam waist w_{0e} at the focal point (~ 16 µm) such that the mid-IR radiation could be concentrated on top of the MRR. An alignment visible laser embedded in the mid-IR source head allowing the beam to be positioned at the center of the ring resonator. This in turn maximizes the strength of the temperature rise in the analyte. The excitation source was operated in pulse mode, with a pulse rate of 25 kHz.

The otpical output signal at the telecoms wavelength from the MRR was coupled to a an InGaAs photodetector. The signal from the detector was sent to a lock-in amplifier (LIA), with a time constant of 100 ms, taking the internal pulse trigger from the mid-IR laser as a reference and constitutes the measured PTS signal.

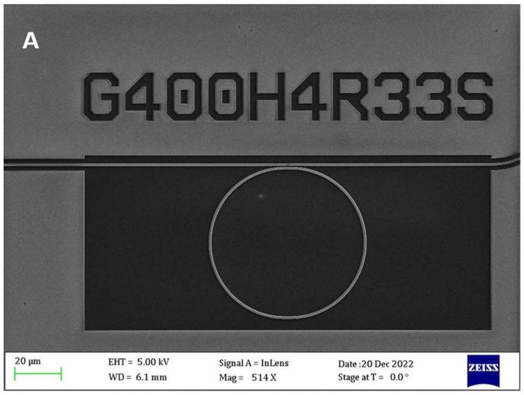

Figure 2. SEM image of the MRR employed for the PTS experiment.

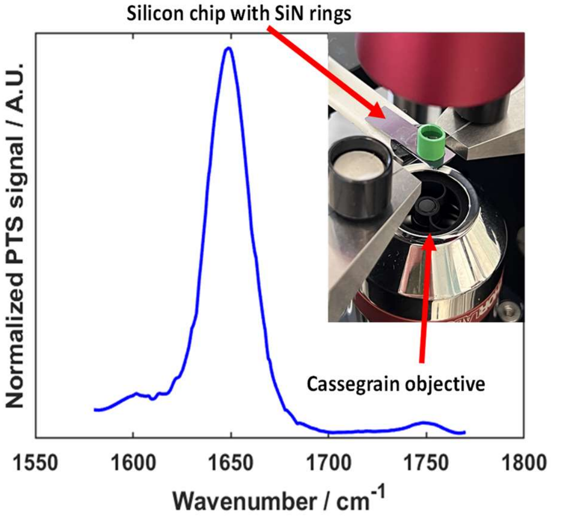

Figure 32. Measurement of water in isopropanol using integrated optics assisted PTS. The analyte is contained in the rubber tube and is excited by a mid IR laser focused by the Cassegrain objective. The ring has a 32µm radius

An example spectrum is shown in figure 3. Savitzky–Golay filtering was additionally performed to remove noise contribution from water vapour absorption.

IV. SUMMARY

In this work, we report on a photothermal micro-ring resonator based sensor for the detection of water in isopropanol. The system is compact and exhi short analysis time, taking a few seconds for a full scan. We have demonstrated that PIC assisted PTS allows for sensor miniaturization by reducing the sample volume. We can cover a broad spectral region, and the technique can be applied to many analytes in both liquid and gas phase. Other transducers may be used offering highly sensitive detection [4].

V. ACKNOWLEDGMENT

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