

# Selective and reversible ammonia gas detection with nanoporous film functionalized silicon photonic micro-ring resonator

Nebiyu A. Yebo,<sup>1,\*5</sup> Sreeprasanth Pulinthanathu Sree,<sup>4,5</sup> Elisabeth Levrau,<sup>3</sup> Christophe Detavernier,<sup>3</sup> Zeger Hens,<sup>2</sup> Johan A. Martens,<sup>4</sup> and Roel Baets<sup>1</sup>

<sup>1</sup>Ghent University-IMEC, Photonics Research group, INTEC, Sint-Pietersnieuwstraat 41, 9000 Gent, Belgium

<sup>2</sup>Ghent University, Physics and chemistry of nanostructures, Krijgslaan 281-S3, 9000 Gent, Belgium

<sup>3</sup>Ghent University, Dept. of Solid State Sciences, COCOON, Krijgslaan 281/S1, Gent B-9000, Belgium

<sup>4</sup>KU Leuven, Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, Leuven B-3001, Belgium.

<sup>5</sup>Contributed equally

\*[nyebo@intec.ugent.be](mailto:nyebo@intec.ugent.be)

**Abstract:** Portable, low cost and real-time gas sensors have a considerable potential in various biomedical and industrial applications. For such applications, nano-photonic gas sensors based on standard silicon fabrication technology offer attractive opportunities. Deposition of high surface area nano-porous coatings on silicon photonic sensors is a means to achieve selective, highly sensitive and multiplexed gas detection on an optical chip. Here we demonstrate selective and reversible ammonia gas detection with functionalized silicon-on-insulator optical micro-ring resonators. The micro-ring resonators are coated with acidic nano-porous aluminosilicate films for specific ammonia sensing, which results in a reversible response to NH<sub>3</sub> with selectivity relative to CO<sub>2</sub>. The ammonia detection limit is estimated at about 5 ppm. The detectors reach a steady response to NH<sub>3</sub> within 30 and return to their base level within 60 to 90 seconds. The work opens perspectives on development of nano-photonic sensors for real-time, non-invasive, low cost and light weight biomedical and industrial sensing applications.

©2012 Optical Society of America

**OCIS codes:** (130.6010) Sensors; (280.4788) Optical sensing and sensors.

---

## References and links

1. V. H. Tran, H. P. Chan, M. Thurston, P. Jackson, C. Lewis, D. Yates, G. Bell, and P. S. Thomas, "Breath analysis of lung cancer patients using an electronic nose detection System," *IEEE Sens. J.* **10**(9), 1514–1518 (2010).
2. G. W. Hunter, J. Xu, P. G. Neudeck, D. B. Makel, B. Ward, and C. C. Liu, "Intelligent chemical sensor systems for in-space safety applications," 42nd AIAA/ASME/SAE/ASEE Joint Propulsion Conf. and Exhibit, Rep AIAA-06-58419(2006).
3. A. B. Kanu and H. H. Hill, Jr., "Ion mobility spectrometry detection for gas chromatography," *J. Chromatogr. A* **1177**(1), 12–27 (2008).
4. V. Ruzsanyi, J. I. Baumbach, S. Sielemann, P. Litterst, M. Westhoff, and L. Freitag, "Detection of human metabolites using multi-capillary columns coupled to ion mobility spectrometers," *J. Chromatogr. A* **1084**(1-2), 145–151 (2005).
5. C. Wang and A. B. Surampudi, "An acetone breath analyzer using cavity ringdown spectroscopy: an initial test with human subjects under various situations," *Meas. Sci. Technol.* **19**(10), 105604 (2008).
6. J. Manne, O. Sukhorukov, W. Jäger, and J. Tulip, "Pulsed quantum cascade laser-based cavity ring-down spectroscopy for ammonia detection in breath," *Appl. Opt.* **45**(36), 9230–9237 (2006).
7. X. Wang, N. Miura, and N. Yamazoe, "Study of WO<sub>3</sub>-based sensing material for NH<sub>3</sub> and NO detection," *Sens. Actuators B Chem.* **66**(1–3), 74–76 (2000).
8. F. Winquist, A. Spetz, I. Lundstrom, and B. Danielsson, "Determination of ammonia in air and aqueous samples with a gas-sensitive semiconductor capacitor," *Anal. Chim. Acta* **164**, 127–138 (1984).
9. S. K. Selvaraja, P. Jaenen, W. Bogaerts, D. Van Thourhout, P. Dumon, and R. Baets, "Fabrication of photonic wire and crystal circuits in silicon-on-insulator using 193nm optical lithography," *J. Lightwave Technol.* **27**(18), 4076–4083 (2009).
10. B. Jalali and S. Fathpour, "Silicon photonics," *J. Lightwave Technol.* **24**(12), 4600–4615 (2006).

11. K. De Vos, J. Girones, T. Claes, Y. De Koninck, S. Popelka, E. Schacht, R. Baets, and P. Bienstman, "Multiplexed antibody detection with an array of silicon-on-insulator microring resonators," *IEEE Photonics J.* **1**(4), 225–235 (2009).
12. N. A. Yebo, D. Taillaert, J. Roels, D. Lahem, M. Debliquy, D. Van Thourhout, and R. Baets, "Silicon-on-insulator (SOI) ring resonator based integrated optical hydrogen sensor," *IEEE Photon. Technol. Lett.* **21**(14), 960–962 (2009).
13. A. Ramachandran, S. Wang, J. Clarke, S. J. Ja, D. Goad, L. Wald, E. M. Flood, E. Knobbe, J. V. Hryniewicz, S. T. Chu, D. Gill, W. Chen, O. King, and B. E. Little, "A universal biosensing platform based on optical microring resonators," *Biosens. Bioelectron.* **23**(7), 939–944 (2008).
14. N. A. Yebo, P. Lommens, Z. Hens, and R. Baets, "An integrated optic ethanol vapor sensor based on a silicon-on-insulator microring resonator coated with a porous ZnO film," *Opt. Express* **18**(11), 11859–11866 (2010).
15. R. Orghici, P. Lützwow, J. Burgmeier, J. Koch, H. Heidrich, W. Schade, N. Welschoff, and S. Waldvogel, "A microring resonator sensor for sensitive detection of 1,3,5-trinitrotoluene (TNT)," *Sensors (Basel)* **10**(7), 6788–6795 (2010).
16. L. R. Narasimhan, W. Goodman, and C. K. N. Patel, "Correlation of breath ammonia with blood urea nitrogen and creatinine during hemodialysis," *Proc. Natl. Acad. Sci. U.S.A.* **98**(8), 4617–4621 (2001).
17. P. Heiduschka, M. Preschel, M. Rosch, and W. Gopel, "Regeneration of an electropolymerised polypyrrole layer for the amperometric detection of ammonia," *Biosens. Bioelectron.* **12**(12), 1227–1231 (1997).
18. A. D. Aguilár, E. S. Forzani, L. A. Nagahara, I. Amlani, R. Tsui, and N. J. Tao, "A breath ammonia sensor based on conducting polymer nanojunctions," *IEEE Sens. J.* **8**(3), 269–273 (2008).
19. R. Lewicki, A. A. Kosterev, D. M. Thomazy, T. H. Risby, S. Solga, T. B. Schwartz, and F. K. Tittel, "Real time ammonia detection in exhaled human breath using a distributed feedback quantum cascade laser based sensor," *Quantum Sensing and Nanophotonic Devices VIII, Proc. of SPIE* **7945**, 79450K.
20. P. H. Rogers and S. Semancik, "Development of optimization procedures for application-specific chemical sensing," *Sens. Actuators B Chem.* **163**(1), 8–19 (2012).
21. T. Sathitwitayakul, M. V. Kuznetsov, I. P. Parkin, and R. Binions, "The gas sensing properties of some complex metal oxides prepared by self-propagating high-temperature synthesis," *Mater. Lett.* **75**, 36–38 (2012).
22. S. Eslava, M. R. Baklanov, C. E. A. Kirschhock, F. Iacopi, S. Aldea, K. Maex, and J. A. Martens, "Characterization of a molecular sieve coating using ellipsometric porosimetry," *Langmuir* **23**(26), 12811–12816 (2007).
23. A. M. Doyle, G. Rupprechter, N. Pfänder, R. Schlögl, C. E. A. Kirschhock, J. A. Martens, and H.-J. Freund, "Ultra-thin zeolite films prepared by spin-coating silicalite-1 precursor solutions," *Chem. Phys. Lett.* **382**(3–4), 404–409 (2003).
24. G. J. Kramer, R. A. Van Santen, C. A. Emeis, and A. K. Nowak, "Understanding the acid behavior of zeolites from theory and experiments," *Nature* **363**(6429), 529–531 (1993).
25. S. P. Sree, J. Dendooven, D. Smeets, D. Deduytsche, A. Aerts, K. Vanstreels, M. R. Baklanov, J. W. Seo, K. Temst, A. Vantomme, C. Detavernier, and J. A. Martens, "Spacious and mechanically flexible mesoporous silica thin film composed of an open network of interlinked nanoslabs," *J. Mater. Chem.* **21**(21), 7692–7699 (2011).
26. C. E. A. Kirschhock, V. Buschmann, S. Kremer, R. Ravishankar, C. J. Y. Houssin, B. L. Mojet, R. A. van Santen, P. J. Grobet, P. A. Jacobs, and J. A. Martens, "Zeosil Nanoslabs: Building Blocks in nPr<sub>4</sub>N<sup>+</sup>-Mediated Synthesis of MFI Zeolite," *Angew. Chem. Int. Ed.* **40**(14), 2637–2640 (2001).
27. S. M. George, "Atomic layer deposition: an overview," *Chem. Rev.* **110**(1), 111–131 (2010).
28. S. P. Sree, J. Dendooven, T. I. Korányi, G. Vanbutsele, K. Houthoofd, D. Deduytsche, C. Detavernier, and J. A. Martens, "Aluminium atomic layer deposition applied to mesoporous zeolites for acid catalytic activity enhancement," *Catal. Sci. Technol.* **1**(2), 218–221 (2011).
29. C. Detavernier, J. Dendooven, S. Pulinthanathu Sree, K. F. Ludwig, and J. A. Martens, "Tailoring nanoporous materials by atomic layer deposition," *Chem. Soc. Rev.* **40**(11), 5242–5253 (2011).

## 1. Introduction

Optical techniques for the detection of liquid and gaseous analytes are interesting in a wide range of applications. Selective detection and multiplexing are some of the attractive features offered by optical sensors. While optical spectroscopic sensors are mature and widely used, emerging alternative optical technologies are significantly contributing to advancements in the current sensing techniques. Fiber-optic and silicon photonic sensors are examples of such emerging technologies. Compact and inexpensive sensors, more particularly, can play valuable roles in applications such as gas detection. There is a high interest for portable, low cost, fast and reliable gas sensors in a number of industrial and biomedical areas such as point-of-care health monitoring and light-weight industrial sensing [1, 2]. However, due to various limitations in current detection technologies, gas sensors satisfying these requirements are barely available today. While selective sensors can be commonly bulky in size and costly, compact and inexpensive sensors tend to be poorly selective or less sensitive [3–8].

As a result, alternative technologies capable of providing solutions to some of the issues with current systems are sought in the gas sensing community. Silicon photonics is one

promising technological platform in this regard. It makes use of Complementary Metal Oxide Semiconductor (CMOS) fabrication opening possibilities for inexpensive volume production as well as seamless integration with portable electronics [9, 10]. Straight forward multiplexing of sensor arrays on a chip is another potential benefit of the silicon nano-photonics platform for compact multi-gas analysis [11]. One of the silicon photonic components proving to be suitable for sensing applications is an optical micro-ring resonator (MRR) [11–15]. The resonance condition of an MRR shows high sensitivity to small changes in the surrounding refractive index. Enhanced sensitivity and selective gas detection can be achieved by chemical functionalization of the MRR surface [14, 15]. More importantly, unlike the widely used electrical gas sensors which are in general restricted to conductive materials, MRRs can be functionalized with a wide range of materials for selective and sensitive gas detection. Consequently, more complex applications involving simultaneous gas detection, such as odor monitoring, can conveniently be addressed by on-chip photonic gas sensors operating at ambient temperature.

An attractive approach to achieve enhanced sensitivities from MRR based sensors is through application of high surface area coatings [14]. Materials with nano size pores, often termed as micro-porous (diameters smaller than 2 nm) and meso-porous (diameters from 2 to 50 nm), coated on optical MRRs offer significantly high surface area on pore walls for adsorption of gas molecules. As a result of the increase of adsorption capacity, very low detection limits could be attained. For specific gas detection, the surface of the porous coating can be functionalized chemically either directly during synthesis or via post-synthesis modification.

Ammonia detection draws a considerable interest with regard to environmental, industrial and medical perspectives. Ammonia levels in farming areas and industrial workspaces often need to be controlled to ensure occupational health. Allowed exposure limit in such environments is about 20 ppm. On the other hand, breath ammonia has been recognized as a bio-marker for physiological disorders in humans [16]. For instance, a high correlation between blood urea nitrogen (BUN) and breath ammonia level in kidney patients has been reported [16]. The BUN test is currently the standard technique for monitoring kidney patients under dialysis treatment. However, this technique involves an invasive and lengthy laboratory procedure. As a consequence, there has been a growing interest for breath ammonia detection as a fast, real time and non-invasive alternative tool for medical diagnosis and health monitoring [16–19].

Different sensor technologies are available for NH<sub>3</sub> detection in various application areas. NH<sub>3</sub> sensors based on metal oxide semiconductors (MOS) have been frequently reported [7, 8]. Despite the potential for miniaturization and high sensitivities down to 10's of ppb levels, poor selectivity has been a common issue with metal oxide sensors [7, 20]. In addition, most MOS sensors need to be operated at higher temperatures up to 300 °C or higher, hence extra power consumption can also be an issue [20, 21]. Sensors based on conducting polymers have also been demonstrated for sensitive and selective detection of NH<sub>3</sub> [17, 18]. Yet, the performance of such sensors has been limited by noticeably slow reversibility after exposure to NH<sub>3</sub> molecules [17, 18].

Optical and mass spectroscopic techniques exist for NH<sub>3</sub> detection [3–6]. Those techniques provide more reliable and selective measurements. However, the high complexity and large size of spectroscopic sensors obstruct their miniaturization, portability and manufacturing at low cost. Commonly, these sensors are bench-top instruments, thus, being less suitable for portable applications [3–6]. More recently, photoacoustic ammonia sensor based on a quantum cascade laser has also been demonstrated for breath ammonia detection [19]. Nevertheless, this device still remains complex due to the requirement for an expensive light source and phase sensitive (lock-in) instrumentation. With the potential to selectively detect sub ppm - ppb concentrations using chemically functionalized MRRs, silicon nano-photonics gas sensors can take advantage of their miniature feature and potentially low cost CMOS fabrication for portable sensing applications [9–15].

Here we report selective detection of gaseous ammonia with MRRs coated with acidic nanoporous aluminosilicate films. Our early stage  $\text{NH}_3$  sensor presented here shows fast, reversible, and selective response with respect to a potential interfering gas,  $\text{CO}_2$ . We used two alternative approaches to functionalize the silicon MRRs with  $\text{NH}_3$  selective acidic nanoporous aluminosilicate films. In the first route an aluminosilicate microporous film inspired by the synthesis of zeolites was applied [22, 23]. In the second approach, a mesoporous silica film is deposited and functionalized with aluminum using Atomic Layer Deposition (ALD). Fast and reversible response to  $\text{NH}_3$  is achieved and selectivity over  $\text{CO}_2$  is obtained with both types of films. Literature on selective gas sensors on a photonic chip is very limited. To our knowledge, this is a first demonstration of fast, reversible and selective ammonia sensing on a silicon photonic chip using a porous functional coating. The potential of this sensor for a cheap, compact, portable and integrated breath ammonia monitoring instrument is discussed.

## 2. Sensing with microring resonators

The resonance condition of an MRR is determined by the cavity optical path length. Accordingly, a first order approximation of the resonance shift due to variations in the effective index and the cavity physical length can be given by Eq. (1).

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta n_{\text{eff}}}{n_g} + \frac{\Delta L}{L} \quad (1)$$

Where  $\lambda$ ,  $n_{\text{eff}}$ ,  $n_g$  and  $L$  represent the resonance wavelength, the effective index, the group index and the cavity length, respectively.

Of particular interest for this work is a resonance shift mediated through the effective index change of a ring resonator coated with a gas sensitive film. Hence, only the first term on the right hand side of Eq. (1) is needed to describe the corresponding resonance shift.

The micro-ring resonators studied here are coated with porous aluminosilicate films for  $\text{NH}_3$  detection. The combination of aluminum and silicon in an oxide framework gives rise to Brønsted acid sites [24]. Since  $\text{NH}_3$  is a base, it is expected to be strongly adsorbed on these films while acidic gases such as  $\text{CO}_2$  will be less favored. Preferential adsorption of  $\text{NH}_3$  molecules will lead to an effective refractive index change of the coated ring resonator. Fig. 1(a) and (b) show a schematic cross section and a scanning electron microscope image of approximately 100 nm thick mesoporous silica film on a  $5\mu\text{m}$  radius silicon microring resonator, respectively.

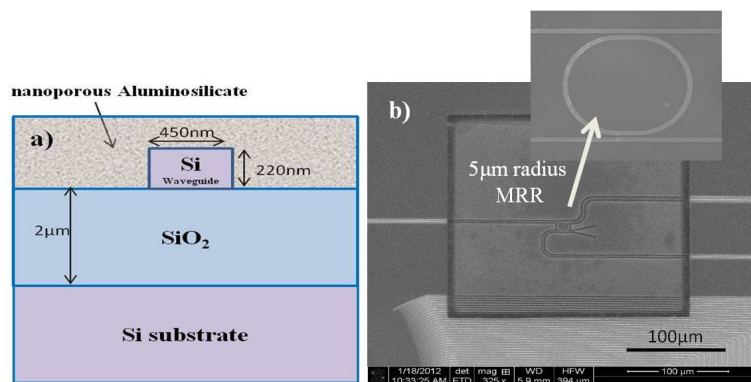


Fig. 1. (a) schematic representation of an SOI microring resonator cross section coated with a porous gas sensitive film (not drawn to scale) (b) Scanning Electron Micrograph of a  $5\mu\text{m}$  radius MRR coated by a mesoporous silica film (thickness  $\sim 100\text{ nm}$ ); Inset: magnified view of the coated MRR.

### 3. Sensor design and fabrication

#### 3.1 Design and fabrication of SOI MRRs

The silicon microring resonators used here for gas detection have a radius of 5  $\mu\text{m}$ , and have been designed for operation in the telecom wavelength range near 1550 nm. The fabrication was done in a standard CMOS fabrication facility as detailed in [9, 14]. In order to localize gas sensitive coatings around the MRRs, the chips were photo-resist patterned. After the coating step, lift-off is used to remove the photoresist.

#### 3.2 Mesoporous silica film deposition

Mesoporous silica films having pore size ca. 12 nm and porosity of ca. 80% were prepared following the synthesis procedure mentioned in [25]. The films were deposited by spin coating a suspension of silicalite nanoslabs [26] combined with Pluronic P123 triblock copolymer which is used as a supramolecular template material to form mesostructures. The nanoslabs are first prepared by hydrolysis of tetraethylorthosilicate (TEOS) in aqueous tetrapropylammonium hydroxide (TPAOH) followed by water addition and stirring for 24 h. This nanoslab suspension was mixed with concentrated HCl and then combined with acidified triblock copolymer solution. The resulting suspension of the nanoslabs and the triblock copolymer was diluted with absolute ethanol and spin coated on photoresist patterned silicon-on-insulator samples. Then the films are hydrothermally annealed at temperatures of 90°C by suspending them in an autoclave above water for 60 h, after which the films are taken out of the autoclave and dried at 60°C. Then the photoresist was removed by a lift-off process and the films were calcined at 350°C to remove the copolymer and the TPA. Afterwards, the films were exposed to ambient air. Typically, 100- 150 nm thick mesoporous films were obtained with this procedure.

#### 3.3 Microporous aluminosilicate film preparation

The preparation of microporous films starts with the synthesis of nanoslabs doped with aluminum through the hydrolysis and polycondensation of TEOS in aqueous TPAOH solution. To introduce Al into the silicate structure, the TPAOH solution is first mixed with appropriate amount of aluminum metal powder. The amount of Al taken was such that the resulting material was expected to have a Si:Al atomic ratio of 100:1. The resulting clear solution was diluted with absolute ethanol and spincoated on photoresist patterned SOI samples. Finally, after the lift-off, the films are calcined at 350°C. Typically, around 100nm thick films are formed. The resulting films are microporous, having pore sizes <2nm and a porosity of ca.45%.

#### 3.4 Aluminum deposition on walls of mesoporous silica films using ALD

Atomic layer deposition of aluminum (Al-ALD) was used to introduce acid sites into the mesoporous films of section 3.2 [27–29]. ALD is a self-limiting thin film growth technique in which a substrate is exposed to chemical precursors and water in an alternating way [27]. The films in this work were treated in a home-built ALD reactor and subjected to 10 ALD cycles. Each ALD cycle involved two subsequent self-terminating half reactions. In the first half reaction, the sample is exposed to trimethylaluminum, TMA [ $\text{Al}(\text{CH}_3)_3$ , 97% purity, Sigma-Aldrich] vapor for 10 seconds, followed by 15 seconds evacuation of the reaction chamber. The second half reaction consists of a 10 second water vapor pulse followed by 15 seconds of evacuation under vacuum. The depositions were done at a temperature of 200°C with TMA/ $\text{H}_2\text{O}$  pressures of 0.3 Pa. Before Al-ALD treatment the mesoporous film was evacuated in vacuo in situ at the ALD temperature. Following the ALD coating of the mesoporous silica the sample was exposed to ambient air prior to the sensing experiments.

### 4. Sensing experiments

An optical setup consisting of a small gas chamber, a tunable laser and an infrared camera is used for the sensing experiments [12, 14]. Before measuring the sensor response to  $\text{NH}_3$  and

CO<sub>2</sub>, reference signals are recorded using pure carrier gas (nitrogen) flowing in the test chamber. Nitrogen is used as a carrier gas to dilute and introduce different concentrations of NH<sub>3</sub> and CO<sub>2</sub> gases into the test chamber. The sensitivity of the sensors to CO<sub>2</sub>, an interfering gas in applications such as breath analysis [6, 16], was investigated in parallel so as to evaluate the selective response toward NH<sub>3</sub>. The recovery of a sensor after exposure to a test gas is evaluated with just carrier gas flowing in the chamber.

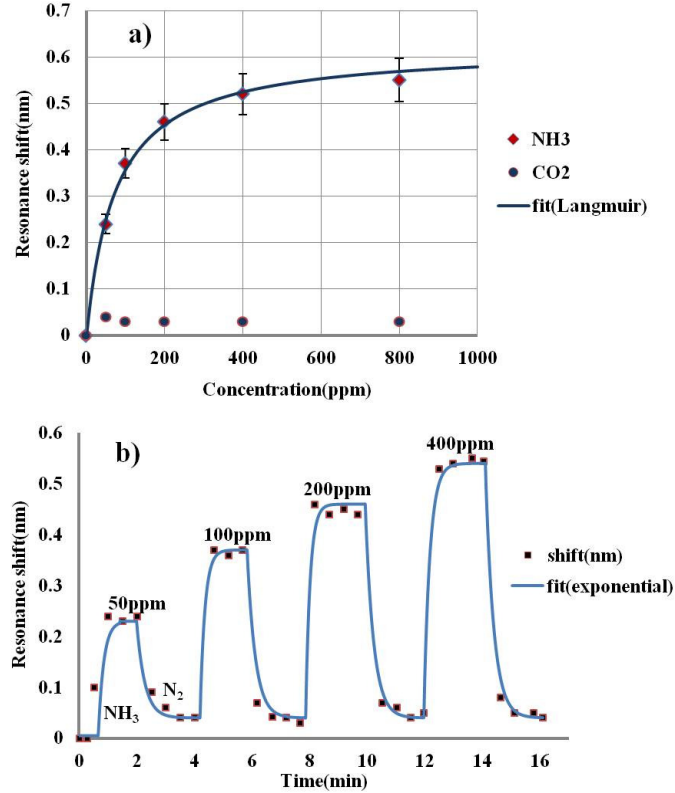


Fig. 2. response from a microporous acidic film coated MRR (a) resonance shift with respect to NH<sub>3</sub> and CO<sub>2</sub> concentrations (b) response and recovery with time at NH<sub>3</sub> concentrations of 50,100,200 and 400 ppm introduced for two minutes.

The resonance shifts of the MRR with microporous aluminosilicate coating upon introducing probe gas into the chamber at different concentration are shown in Fig. 2(a). A well distinguishable sensitivity to NH<sub>3</sub> over CO<sub>2</sub> is observed in 0-800ppm concentration range. The response to NH<sub>3</sub> fits well to Langmuir adsorption isotherm with a linear response extending to 200 ppm [14]. In contrast to NH<sub>3</sub> in the studied concentration range, the response to CO<sub>2</sub> is low and saturates at only ca. 30 ppm. The error bars represent 7-10% standard deviation observed over three measurements taken on the same sample. Interestingly, at a given NH<sub>3</sub> concentration, an equilibrium response is reached in less than 30 seconds while over 95% recovery is reached within 60 - 90 seconds. The response and recovery of the NH<sub>3</sub> sensor with respect to time fitted to exponentials is shown in Fig. 2(b). A slight change of base signal was observed after the first exposure while the responses to later NH<sub>3</sub> exposures almost fully recovered.

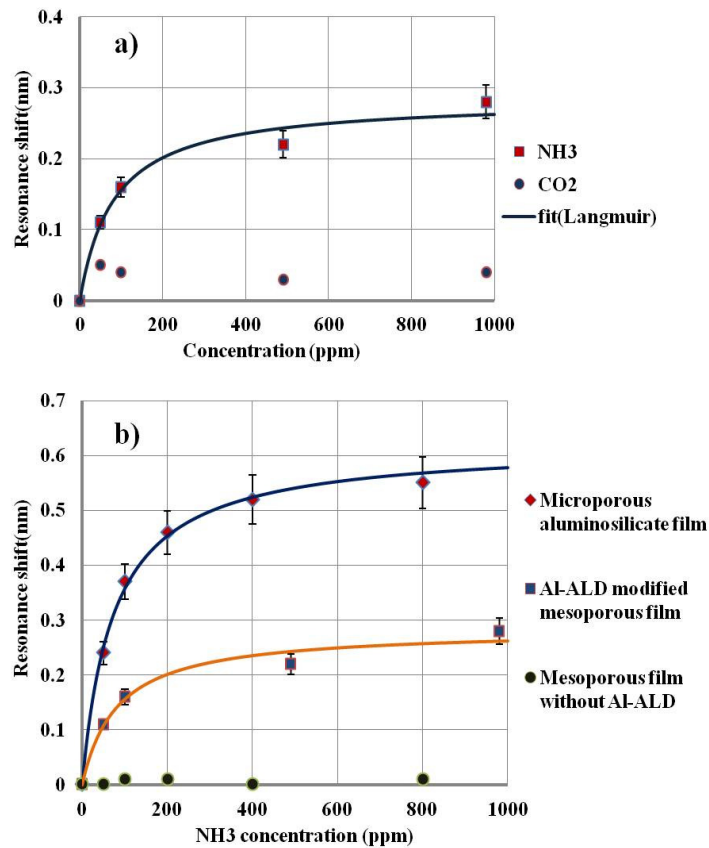


Fig. 3. (a) measured response from mesoporous silica coated MRR upon saturation with NH<sub>3</sub> and CO<sub>2</sub> gases, (b) comparison of NH<sub>3</sub> sensitivity of microporous aluminosilicate film, and mesoporous silica film with and without Al-ALD

As with the microporous coating, a selective response to NH<sub>3</sub> is also obtained using an MRR with mesoporous coating. The corresponding responses to NH<sub>3</sub> and CO<sub>2</sub> gases are shown in Fig. 3(a). In contrast to the microporous film, the Al-ALD treated mesoporous coating showed a lower sensitivity to NH<sub>3</sub>. This can have various reasons, such as a difference in exposed surface area, differences in acidity or hydration level. Further investigations will be needed to identify the critical physico-chemical parameters. The synthesis of porous coatings using the nanoslab approach and the variability of the Al-ALD process will enable fine tuning of the film response. Fig. 3(b) summarizes NH<sub>3</sub> sensitivities measured from the microporous aluminosilicate film, mesoporous silica Al-ALD film, and non-functionalized mesoporous silica film. The bare mesoporous silica coating lacking aluminum showed almost no response to NH<sub>3</sub>. The introduction of aluminum atoms in silicates via direct synthesis in the microporous films or via Al-ALD is responsible for acid sites generation and ammonia adsorption. In agreement with an earlier demonstration [28] our work confirms that acidity is essential for ammonia sensitivity.

The MRRs with nano-porous coating used here have resonance peaks of around 50pm FWHM corresponding to a quality factor of about 30,000. Taking into account this narrow resonance, the sensitivity trend shown in Fig. 2(a), and the CO<sub>2</sub> interference level, a detection limit of about 5ppm is estimated. In this work such a low detection limit has been achieved using the microporous film. For applications such as breath NH<sub>3</sub> monitoring where 0.2 - 2 ppm levels need to be detected, the sensitivity of our sensors could be enhanced by optimizing

the porous films with respect to porosity, Al content and hydrophilicity. The next step in our study will focus on sensitivity enhancement and evaluations against other potentially interfering breath gases. We could observe from our preliminary experiments that the sensors show a measurable response to humidity. This can be attributed to a hydrophilic nature of the nanoporous film surface. However, this issue can potentially be resolved by applying a suitable humidity filter on the gas path [18] or by tailoring the surface hydrophobicity. With continuing developments on compact (on-chip) light sources and interrogation systems, this work demonstrates that subtly functionalized silicon photonic gas sensors show a high promise for portable and real-time sensing applications.

## **5. Conclusions**

Selective gas detection on an optical chip is demonstrated taking advantage of surface functionalized nanoporous silica films on silicon microring resonators. Porous acidic aluminosilicate coatings obtained via deposition of nanoslabs and optionally modified via Atomic Layer Deposition of aluminum demonstrated selective, reversible and fast response to  $\text{NH}_3$  and high selectivity with respect to  $\text{CO}_2$ . Equilibrium response is achieved in less than 30 s and over 95% recovery within 90 s. A detection limit of 5ppm is estimated. A further improvement of the sensitivity could be achieved by optimizing the porosity and surface properties of the porous aluminosilicate films. This work demonstrates the high potential of on-chip optical gas sensors for ultra portable and low cost gas detection in a wide range of applications.

## **Acknowledgments**

Roel Baets, Johan Martens, Sreeprasanth Pulinthanathu Sree, and Nebiyu A. Yebo acknowledge the Flemish government for long-term structural funding (Methusalem). These authors also acknowledge the European Council (ERC)- Inspectra project for funding. Christophe Detavernier and Elisabeth Levrau acknowledge the Fonds voor Wetenschappelijke Onderzoek Vlaanderen (FWO) and the European Research Council (ERC) for funding. Zeger Hens and Christophe Detavernier acknowledge the FWO-Vlaanderen for funding (project nr. G077012).