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Dye-Based Photonic Sensing Systems

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Abstract

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Keywords: photonic sensor; dye thin films; gas sensor; UV sensor; room-temperature wafer level packaging

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1. Introduction

New and improved optical sensors for environmental monitoring and gas sensing offer a number of attractive features including good sensing capabilities, interference immunity and safety [1]. Fiber optical sensors specifically may be used in environments in which the use of electrical sensors is not allowed (e.g. for explosives) [2]. They also allow distributed sensing, but their manufacturing often presents challenges because of its serial nature. Wafer-scale processing and packaging of optical sensor chips offers better economy. In this context, optical dye-based sensing principles present an interesting alternative. However, the methods used for synthesis of active dye thin-films containing a chromophore molecule have previously not been well developed [3]. In general, the methods for preparation of organic nanostructured dye thin-films and other related nanostructured organic or hybrid materials with photonic functionalities are based on wet chemical methods. They are not always straightforward and environmentally friendly. In addition, the integration of optically active dye thin-films with photonic sensing structures is challenging because of the optical coupling requirements and the need for interaction with the environment. These shortcomings have restricted the development of dye-based optical sensors and limited their viability for high-volume applications.

In this work, new types of luminescent thin-films have been prepared by remote plasma assisted vacuum deposition (RPAVD); a new plasma deposition technique that combines plasma polymerization processes with the remote vacuum sublimation of organic dyes. Very flat thin-films with a high concentration of fluorescent dye molecules can hereby be obtained [3–6]. The resulting hybrid thin-films are characterized by well-defined n and k values and the preservation of the photonic properties such as the luminescence of the dye molecules. This is in strong contrast to the properties of films deposited using conventional plasma enhanced CVD or polymerization methods, in which the all the precursor molecules are fragmented, and the obtained thin films do not preserve the structure and functionalities of the starting precursor molecules.

In the sensor systems presented in this work, the dye thin-films are integrated on top of the photonic structures, consisting of vertical resonant cavities (VCs), tuned to the characteristic fluorescence wavelength of the dye thin-films. Sensing transduction results from the changes in the luminescence intensity at this wavelength due to the dye thin-film interaction with the medium.

For accurate detection, it is essential to achieve good coupling of the dye thin-film to the photonic structure. At the same time, the active parts of the sensor system have to be accessible to the sensing medium (e.g. the gas or UV light), while simultaneously be protected against potential harsh environmental influences (e.g. dust, contamination, corrosion, mechanical damage, etc.). Achieving this in an economical way requires wafer scale fabrication and system integration, including a versatile and robust packaging procedure. Sensor packaging is a costly stage of the manufacturing process and is crucial for reliability, yet often the package is part most likely to fail or negatively influence the system response [7]. Implementing wafer-level packaging can reduce the cost and allow very high integration densities for the complete system. Currently, low temperature wafer-level packaging methods predominately use polymer adhesives such as UV curable resins [8], BCB [9] and underfills [10–12]. However, dye thin-films can be affected when they get into contact with polymers or solvents that are typically used for wafer-level packaging.

Additionally, polymers may absorb or react with the analyte gas, thus making them unsuitable for use inside the sensor compartment where the supply of the analyte may be restricted and analyte scavenging reactions could locally reduce the analyte concentrations. This problem can be overcome by exclusively using non-reactive materials, such as metals, inside the sensor cavities [11–14]. For the photonic sensors realized here, a room-temperature wafer-scale packaging approach is utilized [15]. The sensor cavity is sealed by a plastically deformable metal gasket in combination with a room-temperature curable epoxy outside the sensor cavity to provide the permanent bond between the parts of the package.

The optical sensing systems for environmental NO₂ sensing and for sunlight ultraviolet light (UV) A+B sensing used here are the first sensing systems that integrate luminescent thin-film active sensor elements which are formed by dye molecules embedded in a solid plasma polymeric matrix matrix, together with photonic structures. The measurement principle of the sensors is demonstrated by laboratory experiments, and experiments in a real world setting illustrate the practical utility of the sensing systems.

2. Concept of the dye-based sensor system

2.1. Transduction principle of the dye-based photonic sensors

The design of the dye-based photonic sensors relies on vertical resonant cavities acting as selective transducers of the fluorescent emission that is generated by the dye thin-film upon excitation. The working principle is schematically described in Fig. 1. The vertical resonant cavity covers the whole wafer surface, whereas the sensing areas are defined by the selective deposition of dye thin-film on parts of the resonant cavity surface.

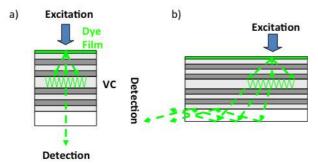


Fig. 1. The principle for the dye-based sensors: a) In UV detection, the detector is behind the chip, b) For NO_2 sensing, the dye thin-film is supported on the VC and the luminesence is detected at the edge of the chip. The substrate is then used as waveguide for the fluorescence signal.

In the case of UV radiation sensing, the radiation excites the dye thin-film and causes fluorescent emission. The fluorescence is selectively transmitted by the vertical resonant cavity, which is tuned to the luminescence wavelength. The sensor read-out takes place at the backside of the chip.

For the NO₂ sensor, an external light source (e.g. a LED) excites the dye thin-film, which then generates an emission that is correlated to the NO₂ level because of the fluorescence quenching of the dye emission. The glass substrate acts as a waveguide, guiding the emission to the chip edges, where it is detected. The sensor response of the final device can optionally be further enhanced by covering the back-side of the glass substrate with a thin reflective layer.

The vertical resonant cavity designs in the sensing systems shown in Fig. 1, consist in a Fabry-Perot resonant cavities adapted to the fluorescence of the dye thin-film materials. The resonant structure incorporates an optical defect in a periodic 1-D photonic crystal creating a photonic bandgap. The defect is equivalent to the cavity in a conventional Fabry-Perot resonator. The cavities are defined by a 1-D periodic distribution of stacked thin layers of SiO₂ and Si₃N₄ with different refractive indices forming distributed Bragg reflectors (DBRs). The defect is formed by a cavity layer with a larger thickness than that of the distributed Bragg reflector layers. This resulting resonant peak in the transmission can be chosen to the wavelength where the dye emission is strong and well correlated to the quantity to be sensed. Also the number and thickness of the stacked layers can be selected to result in the targeted Q-factor.

The dye molecules selected in this work for the dye thin-films are Perylene (PE) for NO₂ detection and Hydroxyflavone (3-HF) for UV detection. The excitation wavelength of PE is between 400 and 480 nm, resulting in a broad emission with maximums at about 490 and 510 nm. The excitation wavelength of (3-HF) is between 300 and 380 nm and the emission wavelength is also around 500 nm. As the thickness of the dye thin-films is in the range of 100 nm, the layers do not show interferences in the visible range, giving a spectrum of the emitted light accurately reflecting the light emitted by the dye molecules.

2.2. Sensor arrangement for NO₂ detection in polluted air

The sensor design for the environmental NO2 sensor system is according to Fig. 1b and the excitation and detection setup is shown in Fig. 2. As illustrated in the figure, this portable sensing platform incorporates a top-side surface illumination source, consisting of a UV LED. The electronic read-out is a 4–20 mA current loop, compatible with industrial control instruments used for tunnel safety management. A filter suppresses excitation wavelengths close to the dye fluorescence emission. To increase the signal to noise ratio, a 9 mm diameter aperture lens with 12 mm focal length is used to focus the excitation light on the centre of the chip, containing the sensing dye thin-film. This leaves a shadowed area at the edges where the detection takes place.

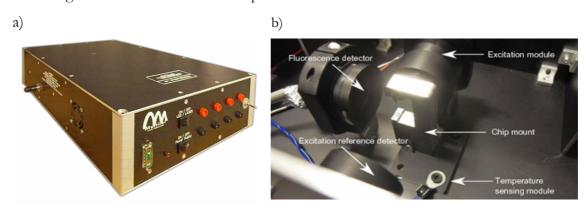


Fig. 2. a) Platform demonstrator for NO_2 detection showing the gas inlet at the left side panel and various signal outputs (including 4-20 mA) on the front panel. b) Optical setup inside the measurement platform.

2.3. Sensor arrangement for UV detection of sunlight

The design for the UV sensor system is according to Fig. 1a. To detect UV radiation, the top panel of the platform demonstrator is replaced by a panel with an aperture and two UV

band-pass filters (Edmund #46-048 and Spectrogon SP-0400) above the sensing chip to remove the strong visible components of sunlight. The vertical resonant cavity chip with the dye thin-film is mounted directly under the UV filters and the fluorescence is detected on the backside of the chip.

3. Design, fabrication, and integration of the dye-based sensor systems

3.1. Dye thin-film deposition

The thin-films for NO₂ sensing are deposited by a RPAVD deposition of PE dye and Adamantane precursor molecules. This technique allows a high concentration of dye molecules to remain intact within a matrix formed by molecular fragments of the same dye and Adamantane generated by interaction with a remote microwave plasma discharge. A cross-linked organic thin-film results, where the PE dye is homogeneously distributed without forming dye aggregates [5].

The UV-sensing thin films are synthetized from 3-HF and Adamantante by the RPAVD technique. The thin-films show an intense green light emission when excited in the UV A+B region, and they are completely transparent in the visible region [16]. All dye-containing polymer thin-films were deposited at room temperature conditions and at wafer scale, using shadow masking for pattering. More details about the synthesis and optical properties of the sensing dye thin-films can be found in the references [3–6,17,18]

3.2. Design of the vertical resonant cavities

The characteristic emission wavelengths of the dye thin-films (PE and 3-HF) are around 500 nm, as described in section 2.1. The resonant peak of the vertical resonant cavities must be tuned to permit selective transmission of the emitted light at the correct wavelengths, and the Q-factor of the cavities should be selected to achieve a good compromise between the sensitivity and the specificity of the sensor systems. To find the best compromise, the optical response was simulated and compared with the luminescence spectra of the dye thin-films. To illustrate this process, measured transmission spectra of two different structures, intended to couple with the NO_2 and UV signals, respectively, are presented. The two vertical resonant cavities consist of 18 pairs of oxide-nitride layers (SiO₂ thickness = 100 nm and Si₃N₄ thickness = 65 nm) on both sides of a Si₃N₄ defect layer; whose thickness is selected to match the resonant mode of the the structure with center of the emission band of the dye film.

The transmission spectra of the structures conceived for UV (a) and NO_2 (b) sensing are shown in Fig. 3 in comparison with the emission spectra of the respective bare luminescent films. The plots show that the resonant peaks of the vertical resonant cavities are tuned to the position of the corresponding luminescence maxima. Following this design principle, a set of vertical cavities were fabricated and tested. The incorporation of a backside reflector was also implemented as an option for some of the structures.

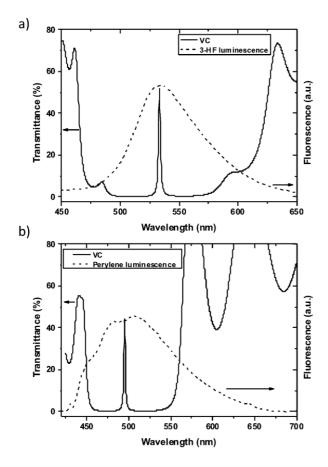


Fig. 3. Measured transmission spectra of vertical resonant cavity (VC) designed for a) UV sensing and b) NO_2 sensing. The fluorescence spectra of the dye thin-films are included in the figures for comparison.

3.3. Fabrication and packaging of the sensor chips

For the applications targeted in the present work, the sensor packaging must fulfill the following requirements: (1) The packaging process must be conducted at near room temperature to avoid damage to the dye thin-films. (2) The package has to be UV-transparent to allow excitation of the dyes. (3) The package for the NO₂ gas sensor application must allow gas diffusion to the dye thin-films. (4) The package for the NO₂ sensor must not have any polymer surfaces exposed to the inside of the package cavity to prevent contamination of the dye thin film or NO₂ scavenging. (5) The dye thin-film surfaces must be protected against dust.

The overall wafer-scale integration and packaging of the sensor chips is outlined in Fig. 4, and the sensor package is schematically shown in Fig. 5. The sensor package consists of a glass cap with a plastically deformable gold gasket that encloses and seals a cavity. The dye thin-film is located on the device wafer inside the cavity. An epoxy underfill is used to provide a permanent bond between the two substrates. When the epoxy cures, it shrinks and creates a compressive force on the gold gaskets, thereby completing the seal.

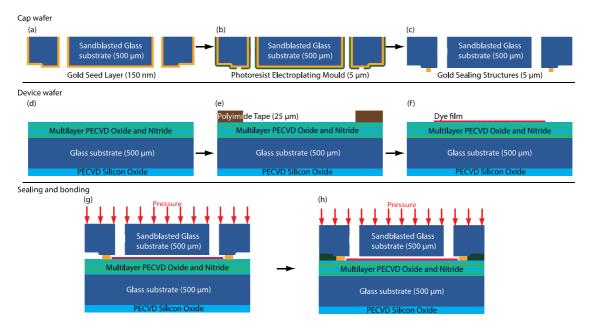


Fig. 4. Outline of the integration and packaging process: The cap wafer (a) to (c) and the device wafer (d) to (f) are processed separately and thereafter aligned, sealed by compression (g) and bonded using an underfill epoxy (h).

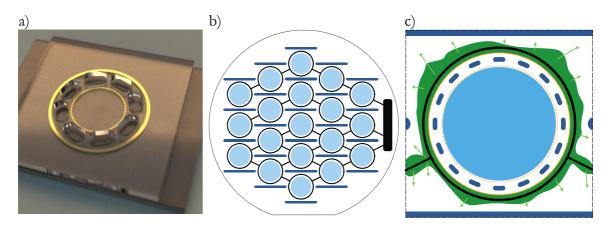


Fig. 5. (a) Computer generated illustration of the package with holes for the NO_2 sensor chip. The package consists of two glass pieces bonded together with epoxy, which is separated from the cavity by gold gaskets. (b) Layout of the underfill distribution channels (black) on the wafer. Through holes in dark blue (dark gray in print) for the filling process, and dye material in light blue (light gray in print). (c) Close-up of a chip, illustrating that the epoxy (green) is first distributed in the channel (black) and then onto the chip. The gold gasket (orange), the optional gold stud filter (dashed orange) and the cavity ventilation are also visible.

For the NO₂ gas sensors, the glass lid is perforated to enable the analyte gas to access the dye thin-film. In the UV sensor, the glass lid does not contain perforations and thus the cavity is sealed to eliminate any gas interaction. An epoxy underfill surrounds the cavity enclosed by the gold gasket and bonds the two substrates together. This design allows efficient room-temperature bonding and sealing of the cavities and at the same time prevents any bonding polymer from getting in contact with the dye thin-films. To allow gas sensing in environments with particle contaminations, the package design of the NO₂ sensor comprises a three-stage filter. The first stage is formed by the 0.5 x 1 mm gas inlet

perforation of the lid. The small distance between the sensing chip and the glass cap chip, which is defined by the gold gasket height, acts as a 1-dimensional particle filter, which is the second stage. A third filter, consisting of closely spaced gold studs, filters smaller particles. Full 3D simulations conducted using Comsol Multiphysics support that the analyte diffusion into the packaged chip closely follows Fick's first law of diffusion. For the dimensions and specific topology of the sensor chips, this means that reaching 90 % of the outside NO₂ concentration at the center of the sensing cavity takes less than 2 s. This is one order of magnitude faster than the expected response time of the dye thin-films [5].

For integration and packaging of the sensors, $500 \, \mu m$ thick and $100 \, mm$ diameter borofloat glass-cap substrates were sandblasted (Little Things Factory GmbH, Germany) to form wafer through-holes the wafer for the underfill stoppers, and to a depth of $100 \, \mu m$ for the underfill channel structures, as shown in Fig. 4a. A 150 nm thick layer of Ti/Au was evaporated for a conductive electroplating base on the wafer surface that contains the channels. To form an electroplating mold, a 5 μm thick AZ 9260 photo resist (Clariant) was spray coated and patterned, as illustrated in Fig. 4b. The mold for the 2 μm wide gold gaskets and filter studs was then filled by electroplating 99.9 % pure gold (EnthoneMicrofab Au 660). The resist mold and the plating base were finally removed by oxygen plasma and wet etching in KI (aq.) and H_2O_2 , as shown in Fig. 4c.

The device wafers, also 500 µm thick and 100 mm diameter borofloat glass, were first cleaned in a boiling piranha solution and rinsed in deionized water. The Fabry-Perot resonator consisting of a multilayer silicon oxide and nitride thin-film stack was deposited using plasma enhanced CVD in an Oxford Plasmalab 80+ reactor (Fig. 4d). The entire deposition process was completed in one vacuum cycle at a chuck temperature of 300 °C. To avoid wafer bending due to the thermal expansion mismatch of silicon dioxide and the glass substrate, a SiO₂ layer with the same thickness as the total thickness of the front side stack, was deposited on the backside of the glass wafer, as schematically depicted in Fig. 4d. For patterning the subsequently deposited dye thin-film, a 25 µm thick polyimide adhesive tape that had been patterned in a cutting plotter, was attached to the wafer, as shown in Fig. 4e. As indicated in Fig. 4f, the UV or NO₂ sensing dye thin-films were deposited directly onto the wafers using room-temperature remote plasma deposition. The targeted thickness of the resulting dye layers was 100 nm, which was controlled by using a quartz crystal monitor that is placed in the deposition chamber [3,4,18].

After completing the fabrication of the device and the cap wafers, the wafers were manually aligned under a stereomicroscope, according to the layout in Fig. 5b allowing access to the epoxy underfill reservoir after the wafer stack was clamped together. The stack was mounted in a Süss Microtec CB8 wafer bonder that applied a tool force to the wafer stack to compress the gold gaskets, as depicted in Fig. 4g. With the wafers still under tool pressure, 3 ml of low viscous epoxy underfill (Epotek 301, Epoxy Technology) was dispensed in the reservoir. The epoxy was cured for 16 hours at room temperature. To increase the underfill rate and to achieve a complete coverage of the low viscosity underfill epoxy over the whole wafer with a single injection point, a microfluidic network was implemented [12,19]. This underfill process was designed to occur in two phases. First, a network of 100 µm high microfluidic channels was filled by capillary forces. As shown in Fig. 5b, this network is connected to a single reservoir and surrounds all the zones of the wafer covered with the dye thin-films. Simultaneously, the gap between the two wafers,

which is on the order of 3 µm, defines the second phase of capillary driven filling, as shown in Fig. 5c. The epoxy spreads from the channels towards the wafer gap, stopping on the through-etched glass sections, which act as fluidic barriers. These through-etched sections also allow air to escape, facilitating a void-free underfill process. After this second and slower filling phase is finalized, all the chips are completely bonded and sealed at wafer-scale. After the sensor system packaging is completed, a reflective layer of 50 nm aluminum is optionally sputtered on the backside of the bonded device wafer. The sensors were finally diced upside down using a wafer saw. Fig. 6 shows a picture with a finalized UV sensor chip and a finalized NO₂ sensor chip after the dicing. At this point it is important to stress that all the different fabrication stages are carried out at wafer level allowing for the mass production of inexpensive and even disposable photonic sensor chips.

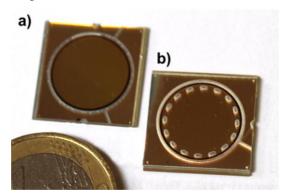


Fig. 6. Packaged devices after wafer scale fabrication and dicing: (a) UV and (b) NO_2 sensing chips.

4. Experiments and characterization of the dye-based sensor systems

4.1. Characterization of the dye-based sensing structures and coupling of the luminescence signal

The photonic properties of the vertical cavities were specifically adapted to the luminescent characteristics of the two types of sensors films. Thus, by assembly of these two components we fabricated luminescent photonic chips with tailored luminescent properties and enhanced sensing performances. Fig. 7 compares the emission spectra of reference dye thin-films, deposited on fused silica, with the luminescent output signal of the sensor chips detected through vertical cavities as shown in Fig. 1. The graphs show that the broad emission band of the dye thin-film is converted into narrow peaks at the resonant modes of the vertical resonant cavity. These narrow peaks are used to evaluate the sensing response. With this approach, a rather monochromatic (FWHM < 5 nm) luminescent signal is obtained that can be much easier handled in the detection system. The inherently filtered lateral emission detected at the chip edges is illustrated in Fig. 7b. The graph shows that the analyzed signal corresponds to the out-of-normal fluorescence emission modulated by the photonic structure and laterally guided through the waveguiding glass substrate. Since the excitation beam impinges normal to the surface, this detection configuration filters the excitation beam and improves the signal to noise ratio. In addition, this configuration enables independent monitoring of the excitation beam with a second photodetector placed behind the sensor.

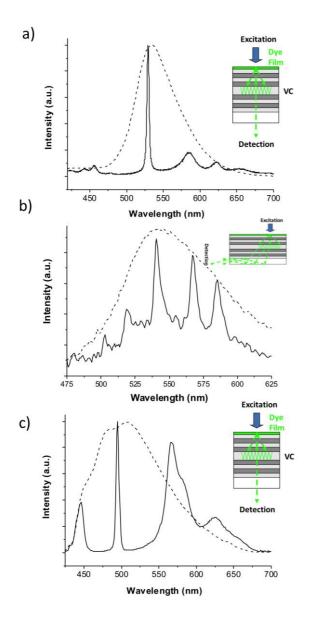


Fig. 7. Luminescent responses of the dye thin-films deposited on the vertical cavity structures. The reference emission spectra of the corresponding luminescent thin-films deposited on glass are included in the figures. These measurements were carried out as indicated in the insets: (a) Emission spectra acquired at the backside of the photonic substrates of a 3-HF thin-film. (b) Lateral emission at the chip edge of the 3-HF thin-film. (c) Emission spectra through the photonic structure of the NO_2 sensing thin-film.

4.2. Measurement results from the dye-based sensor systems

NO₂ and UV detection experiments were carried out both in the laboratory and in real-world scenarios. For the latter, the packaged sensor chips together with the measurement platforms described in sections 2.2 and 2.3 were used. The sensors were evaluated for NO₂ detection in car traffic tunnels and for sunlight UVA+B intensity monitoring.

4.2.1 NO₂ gas detection in polluted air

Experiments were carried out with bare PE dye thin-films to qualitatively assess the evolution of the fluorerscence properties upon exposing them to NO₂ concentrations in a car traffic tunnel. For these assessments, several PE thin-films were placed in perforated metallic boxes and exposed to the environment in the car traffic tunnel for a time range

between one and seven days. Before the exposure to the tunnel environment, all the samples had identical luminescent properties. Fig. 8 compares the emission spectra of the exposed samples with that of a reference sample stored in the laboratory under NO₂-free conditions. The results clearly show the gradual quenching of the fluorescence emissions with prolonged exposure to the polluted environment. The result is in line with previous studies showing that this type of PE thin-films act as accumulative sensors during NO₂ detection [4,5].

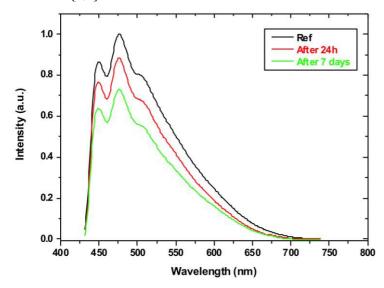


Fig. 8. Emission spectra of the PE thin-films after their exposure between one and seven days to the NO_2 in the environment of a traffic tunnel with respect to a reference sample stored in the laboratory.

To test the functionality of the NO₂ sensor in the portable measurement platform, a set of experiments were carried out in the laboratory. Fig. 9a shows the results of one of these experiments, corresponding to the detection of 10 ppm NO₂ in air. The relatively high concentration was chosen to speed up the characterization time in the experiments. The plot clearly shows that the output signal progressively decreases with the exposure time, which is due to the quenching of the fluorescence emission of the active layer by reaction with the NO₂. This type of integral curves can be used to derive differential response curves to estimate the actual average NO₂ concentration during defined periods of time.

The NO₂ gas sensing systems were finally tested in a car traffic tunnel in Valencia, Spain. The measurements were carried out after calibrating the measurement system with the reference data acquired under controlled conditions in the laboratory. The measurement platform, containing the sensor chip, was placed next to an existing commercial NO₂ sensor (Model DF-9200 from MSA) for these experiments. Although the comparative study presented here corresponds to periods of only 2–3 hours, the measurements are consistent with the data registered in a longer experiment that was lasting for 30 days. Fig. 9b shows the measurement data of the dye-based photonic sensor and the existing commercial sensor during rush hours, when the NO₂ concentration reaches maximum values. The measurement data of the photonic platform is reasonably stable and in line with the data provided by the commercial sensor. Agreement between the demonstrator and commercial sensor readings is also observed for low NO₂ concentrations shown in Fig. 9c, thus indicating that the system is sufficiently sensitive for these low analyte levels. For a dynamic NO₂ signal, the response of both detectors in a situation of increasing traffic is

compared. Particularly, Fig. 9 shows the data registered early in the morning just before rush hour, when the NO₂ concentration increases from 1.5 ppm to 2 ppm. From this figure it is apparent that the concentration values provided by the photonic dye-based sensor gradually increase, as do the registered concentrations of the commercial sensor and that the photonic system has a similar reaction time. Despite the discrepancies observed in the absolute values, the almost parallel responses of our prototype and the commercial device validate the detection principle proposed in the present work.

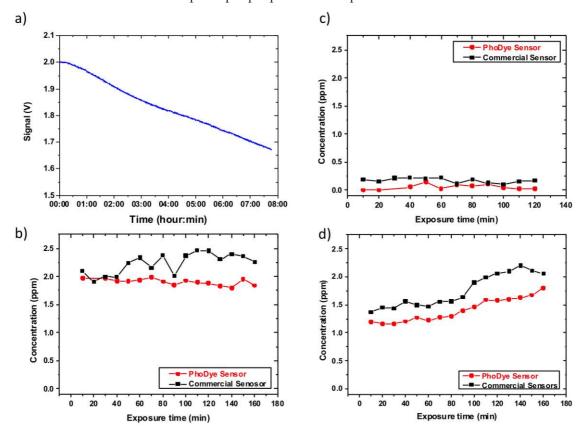


Fig. 9. (a) Measurement of a 10 ppm NO_2 flow in a laboratory experiment. (b)-(d) Measurements of NO_2 concentrations in a traffic tunnel. The graphs compare the measurement data of the dye-based photonic sensor system and a commercial sensor system during time periods with various traffic conditions: (b) High and stable NO_2 concentration. (c) Low and stable NO_2 concentration. (d) Gradually increasing NO_2 concentration.

4.2.2. Sunlight UV detection

Previous research showed that the 3-HF thin-films emit an intense green luminescence when exposed to UV A+B radiation. The emission intensity is linear with the UV intensity [16–18]. Thus, the green emission can be used to determine the level of UV light irradiating a sample. The UV measurement platform was used to measure UV sun intensity over several time periods. As an example, Fig. 10 shows the output signal recorded on the 25th of June 2010 in Mons, Belgium. For comparison, the UV index values recorded simultaneously by a meteorology station in Soumagne, around 120 km east of Mons [20] is also shown. Note that both data sets depict a similar overall evolution during the 6 hour measurement period, except for some variations due to clouds. The comparable evolution of the two kinds of measurements sustains that the room temperature reversible

fluorescence detection of UV light based on the presented measurement principle is reliable, and can be used for monitoring of UV light under real conditions.

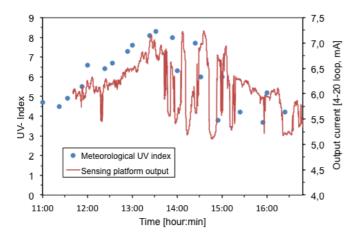


Fig. 10. Output from the measurement platform working with the 3-HF sensor chip for UV radiation detection. The blue dots correspond to the sunlight UV index measured by a nearby meteorological station and the red curve corresponds to the output voltage provided by the photonic measurement platform.

5. Conclusions

In this paper we report on a dye-based photonic sensor platform for UV and NO₂ sensing. For the first time, fully integrated sensing systems based on plasma deposited fluorescent organic nanocomposite thin-films are demonstrated. The fluorescent signal of the dye thin-films responds to changes in the environment and is selectively filtered by a Fabry-Perot resonant cavity photonic structure, onto which the dye thin-film is deposited. The photonic chip thus combines a sensing element and a photonic transducer tuned to the sensing signal in a single package formed at wafer scale.

The sensor systems were evaluated in real-world scenarios in a car traffic tunnel for NO_2 detection and in an open environment for UV detection. The results confirm the suitability of the developed technology for environmental monitoring of different variables. The narrow spectral peaks of the photonic structures are very sensitive to small changes in the wavelength spectral response and intensity of the dye emissions. Thus, the technology is generic and can be expanded to other applications by utilizing different dye sensing elements.

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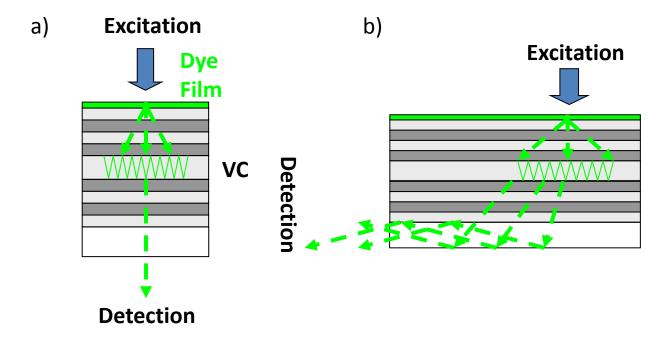


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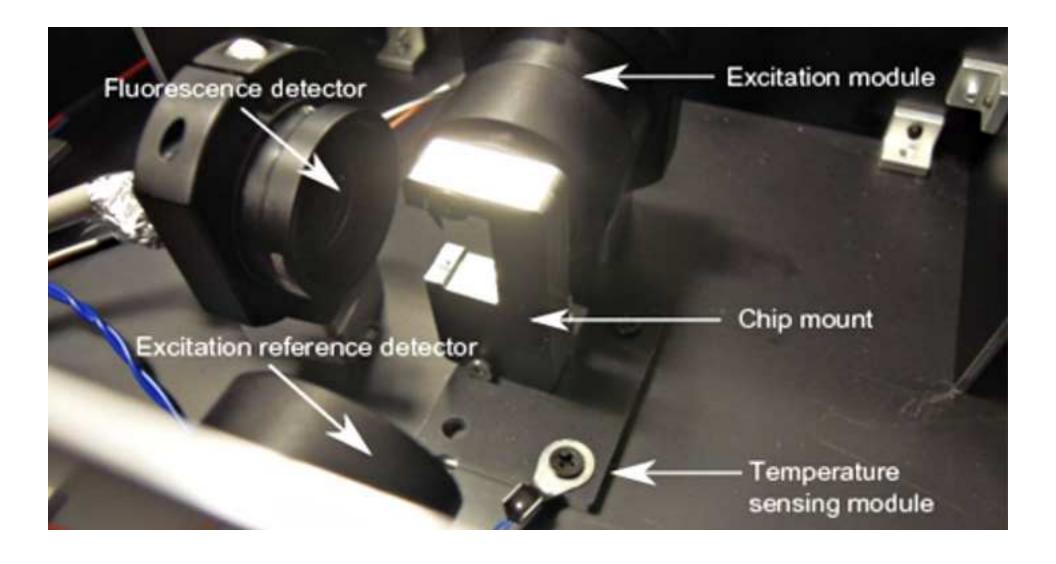
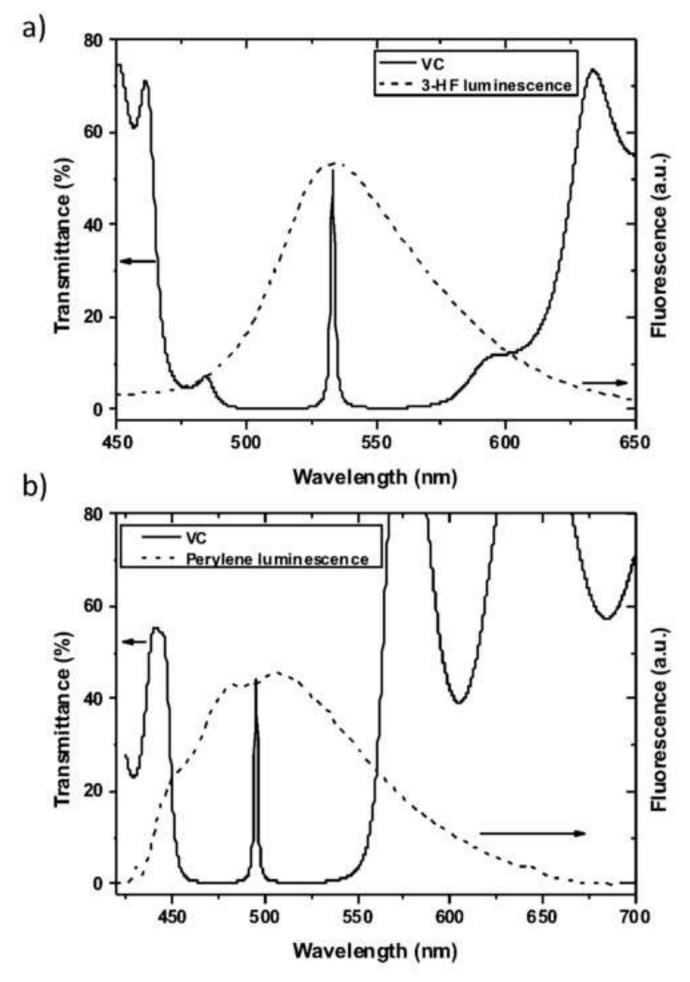


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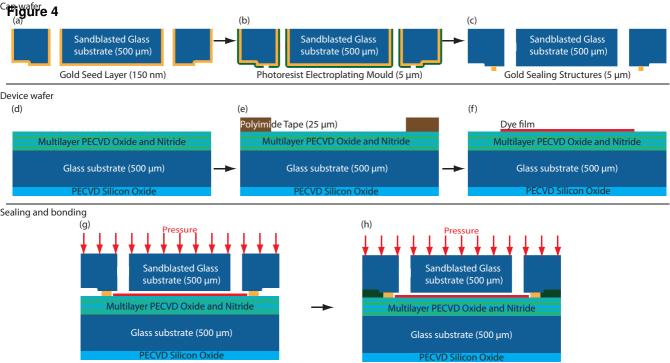
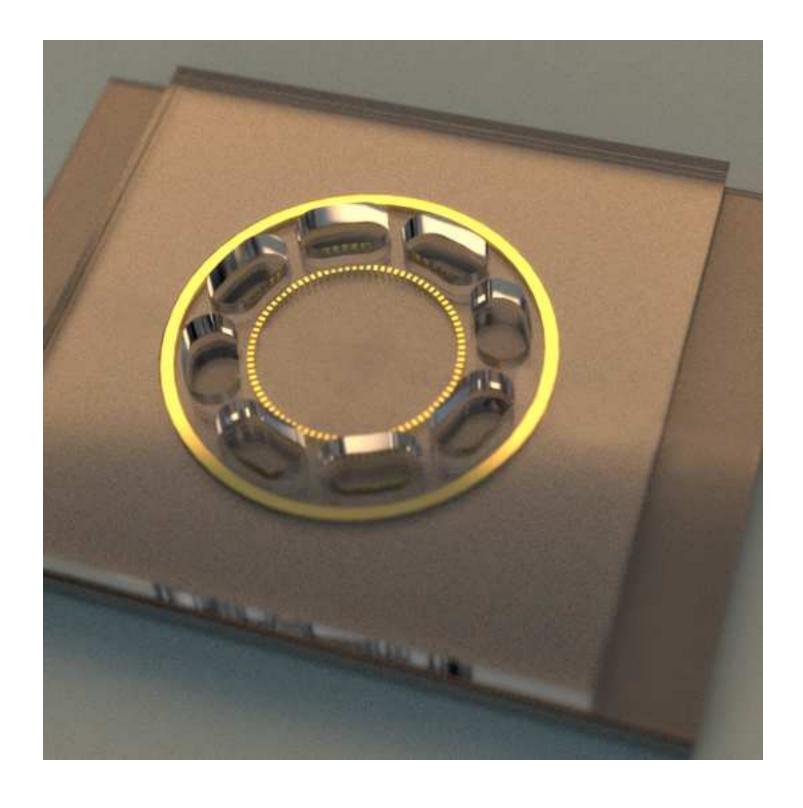
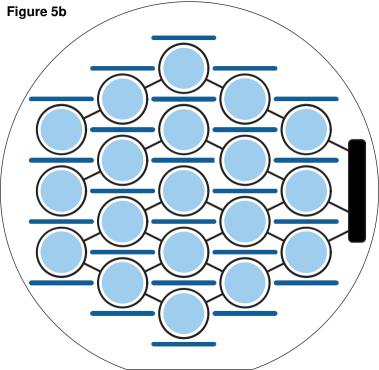


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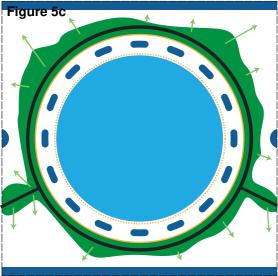


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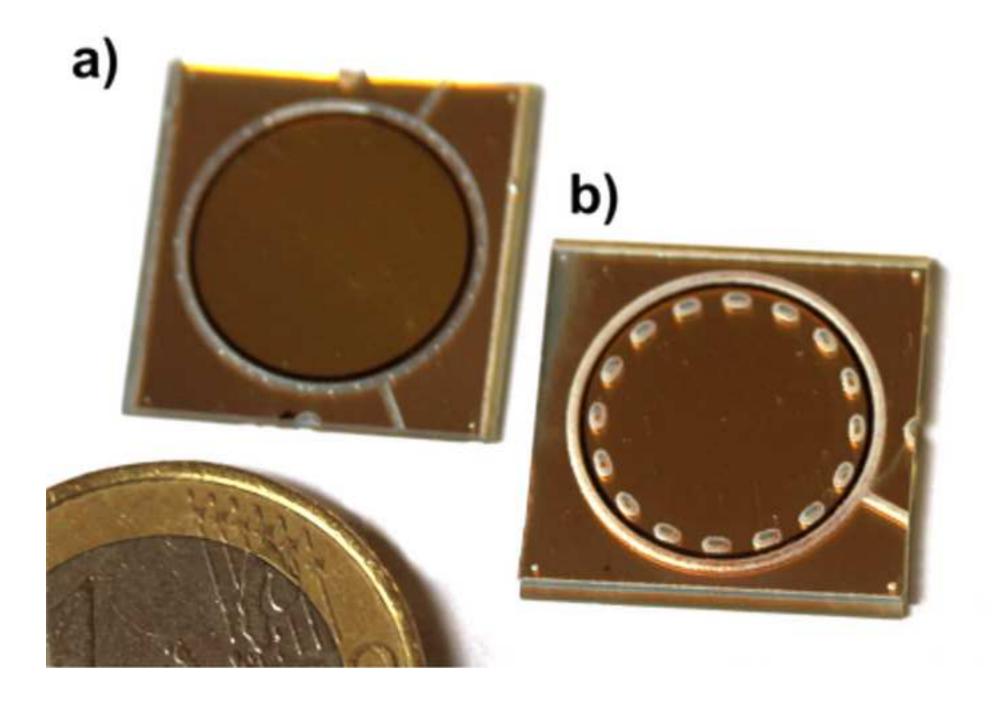


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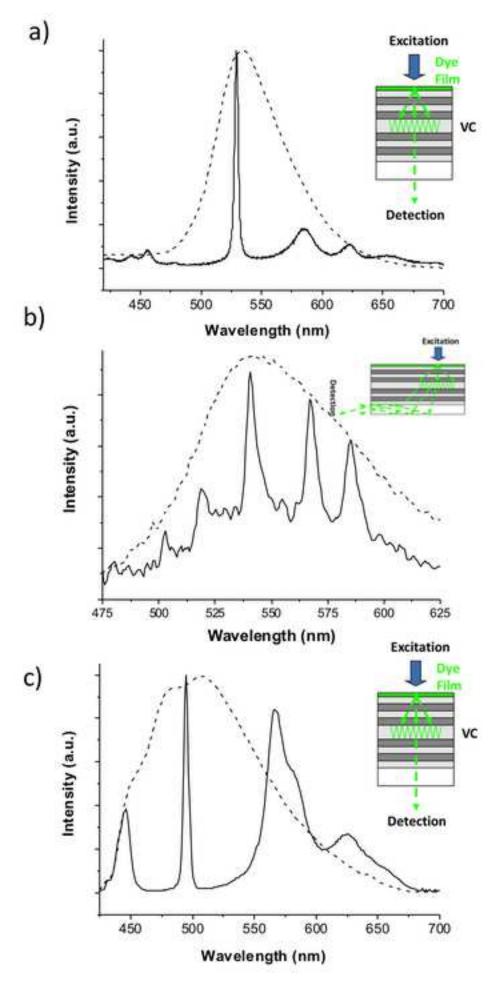


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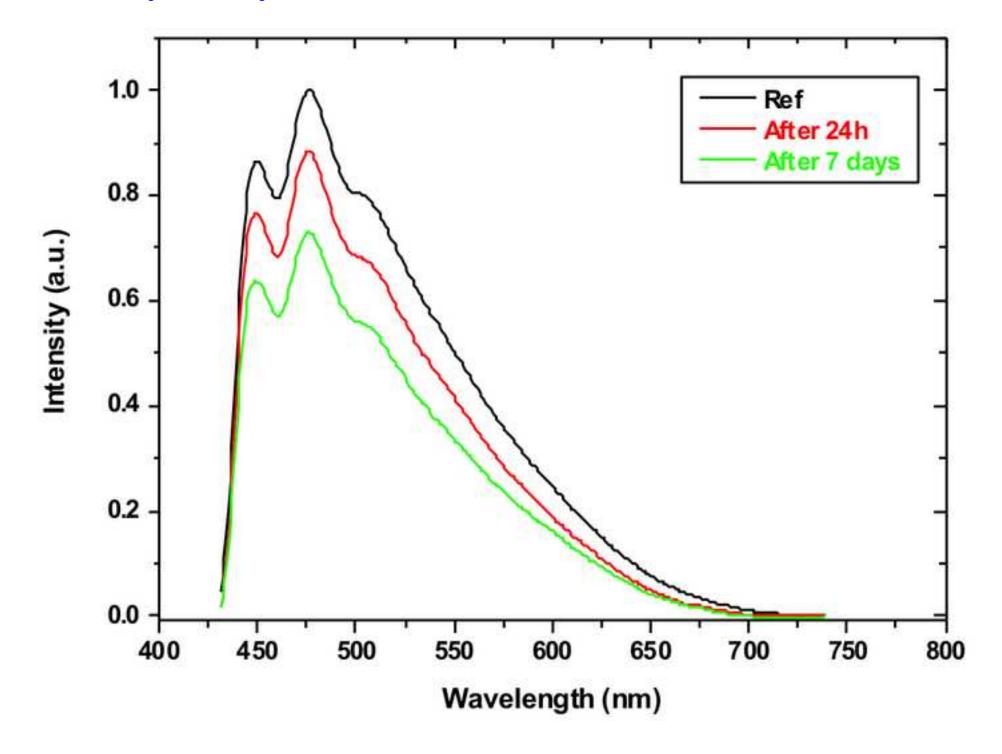
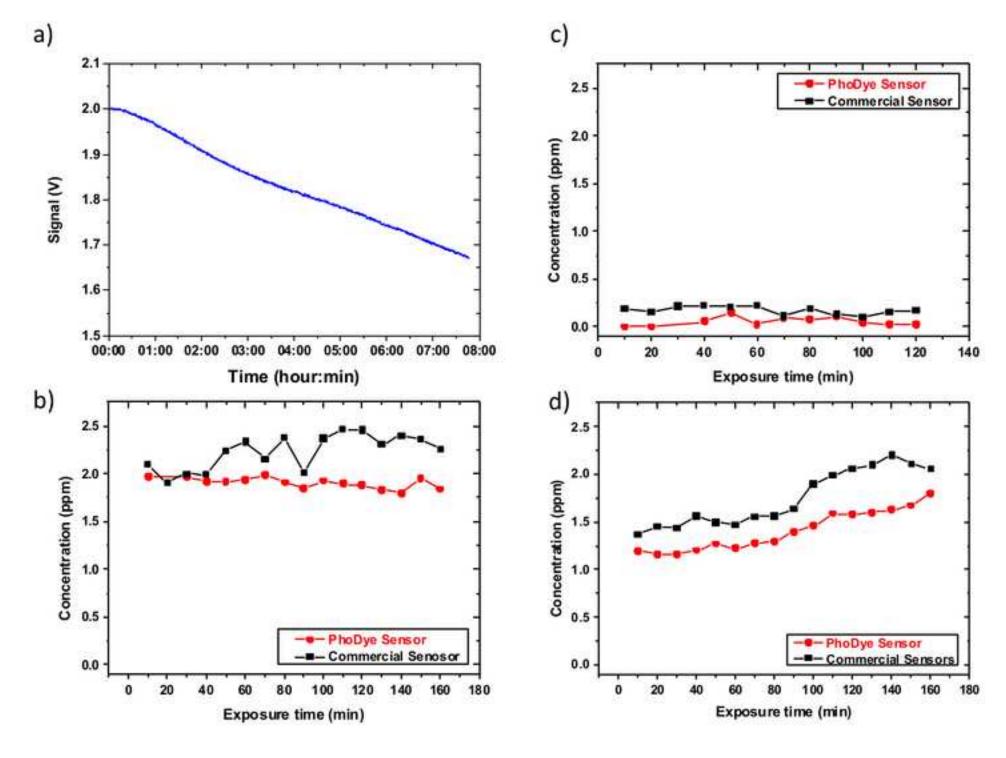
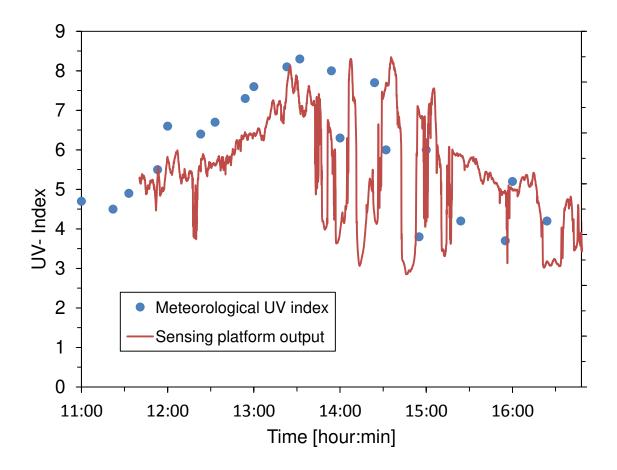


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