A Novel Optochemical Sensor Based on SnO_2 Sensitive Thin Film for ppm Ammonia Detection in Liquid Environment

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***Abstract*—In this paper, a fiber optic sensing system, designed, and developed for the detection of ammonia in aqueous ambient at room temperature, is presented. The sensor is constituted by a standard silica optical fiber (SOF) coated by a tin dioxide sensitive layer. The SnO_2 films have been transferred onto the distal end of the SOF by means of the simple and low-cost electrostatic-spray-pyrolysis deposition technique. The spectral characterization of the fabricated samples has been carried out in the wavelength range 400–1750 nm in order to estimate the thickness of the SnO_2 fiber coatings. The morphology and the elemental composition of the deposited layers have also been investigated by means of scanning-electron-microscopy observation and energy-dispersive-spectrometer analysis, respectively. Single-wavelength reflectance measurements have been carried out to test the sensing performances of the realized sensors toward ammonia traces in water. A fiber-Bragg-grating temperature sensor has also been used for monitoring the temperature changes occurring inside the test ambient during the experimental measurements, in order to identify the effects of thermal drifts on the sensor response. The results here presented demonstrate that the developed refractometric chemical sensor is able to provide measurements of ammonia concentration in water and at room temperature with a high sensitivity, response times of few minutes, and a resolution as low as 2 ppm.**

***Index Terms*—Ammonia detection in water, optical fiber sensors, tin dioxide film.**

I. Introduction

AMMONIA molecules are a nutrient required for life, but excess ammonia may accumulate in the organism and cause alteration of metabolism or increases in body pH. If ingested, by drinking polluted water, ammonia will corrode the lining of the mouth, esophagus, and stomach. Ammonia levels in excess of the recommended limits may even harm aquatic life. Experiments have shown that the lethal concentration for a variety of fish species ranges from 0.2 to 2.0 mg/l [1]. For these reasons, accurate devices that are able to detect very low concentrations of ammonia in water are of great interest in water monitoring applications, especially when continuous and *in situ* diagnosis analyses are required.

In order to detect water ammonia occurring in toxic concentrations, the choice of optical fiber technology combined with optoelectronic methodologies and techniques provides several advantages for the achievement of advanced performances in the monitoring system. As matter of fact, the optical fiber offers the dual role of sensor and data transportation system, it is small in diameter, light, able to measure simultaneously several parameters, resistant to corrosion and fatigue, and capable of high-bandwidth operation. In addition, because of the dielectric nature of the silica optical fiber (SOF), it is immune to external electromagnetic fields and no electrical pathway is created within the host structure. Furthermore, its multiplexing capabilities allow to construct very compact sensors with a reduced number of connections to the instrumentation. On the other hand, in order to develop a sensor able to detect low ammonia concentrations, integration with a suitable sensitive material is strongly required.

Tin dioxide has strongly attracted the attention of the researchers over the last few decades as highly sensitive material for gaseous ammonia detection [2], [3]. Structural, electrical, and optical properties of tin oxide have been investigated by many authors [4]. Tin oxide films have polycrystalline structure with particular crystalline size and surface morphology. In addition, after its deposition, the structure of tin oxide films is stable in a wide range of temperatures 25 °C–500 °C [5]. The conductivity of SnO_2 films has been investigated in dependence on the film thickness and operation temperature. Their electrical properties have been studied at different film temperatures and in presence of different gases. It has been found that adsorption of gas molecules on tin oxide surface leads to changes of resistance that makes possible to use them for gas sensing applications [6]. The tin-oxide-based gas sensors are based on the measurement of resistance changes related to analyte adsorption. In order to get the higher sensitivity, tin-oxide-based sensors usually work at high temperatures (250 °C–450 °C). By adding catalytic dopants (Pt, Pd, Au, and Ag) the operating temperature can be decreased, but it cannot decrease down to the room temperature.

Many technological methods to deposit tin oxide films have been investigated and improved such as magnetron sputtering, sol-gel, chemical vapor deposition, spray, and

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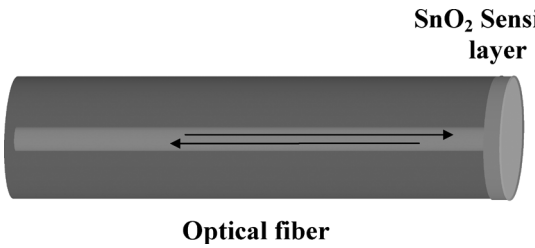


Fig. 1. Schematic view of the exploited optical fiber sensor configuration.

electrostatic-spray-pyrolysis (ESP) methods [7]. They allow obtaining tin oxide layers with different thicknesses, surface morphology, crystalline size, electrical, and optical properties. However, peculiarities of geometrical dimensions of optical fibers make sol-gel, spray, and ESP methods more attractive for the deposition. In addition, ESP is a very simple and inexpensive technique, which allows to change the deposition process parameters, like the metal chloride concentration, the solution volume, and the substrate temperature, in order to tailor the structural properties of the film such as crystalline size, thickness, and porosity [8]. It is worth noting that, in spite of the gas sensing properties showed by tin dioxide-based sensors [6], they have never been used in a liquid environment.

In this paper, the attention was focused in the development of a novel fiber optic sensor able to overcome the aforementioned issues as the high-temperature operation and the impossibility to be used within aqueous environment for *in situ* monitoring [9]. To this aim, an optoelectronic sensor for the detection of ammonia, able to work in water and at room temperature, has been developed. The ESP technique has been used for the tin dioxide films deposition on optical fibers. Spectral characterizations of the fabricated samples have been carried out in the visible (VIS) and near infrared (NIR) regions (400–1750 nm) in order to estimate the thickness of the SnO_2 films. Moreover, a morphological characterization of the deposited layers have been performed by means of scanning-electron-microscopy (SEM) observation and energy dispersive spectrometer (EDS) analysis, respectively. Single-wavelength (1550 nm) reflectance measurements have been carried out to test the sensing performances of the realized sensors toward ammonia. Finally, experimental results demonstrating the capability of the proposed sensor to perform ammonia detection in water with 2-ppm resolution are presented.

II. Methodology

The proposed configuration relies on an extrinsic Fabry–Perót interferometer. With reference to Fig. 1, the principle of operation of the refractometric chemical sensor is based on the fact that the changes in the optical and geometric properties of a thin film deposited upon the distal end of a standard optical fiber modify the power level reflected by the fiber-film interface, in accordance to the following expression [10]:

$$R_{123} = \left| \frac{r_{12} + r_{23} \cdot e^{-i \cdot \beta}}{1 + r_{12} \cdot r_{23} \cdot e^{-i \cdot \beta}} \right|^2 = f(n_{\text{eff}}, n_d, n_{\text{ext}}, d, \lambda) \quad (1)$$

with

$$r_{12} = \frac{n_{\text{eff}} - n_d}{n_{\text{eff}} + n_d};\ r_{23} = \frac{n_d - n_{\text{ext}}}{n_d + n_{\text{ext}}};\ \beta = \left(\frac{4 \cdot \pi}{\lambda} \right) \cdot n_d \cdot d \quad (2)$$

where n_{eff} is the effective refractive index of the fundamental mode of the optical fiber, λ is the optical wavelength, d is the film thickness, n_{ext} is the external medium refractive index, and n_d is the refractive index of the overlayer. The refractive index n_d has been assumed real because the overlayer exploited in this paper is transparent in the considered wavelength range. As a matter of the fact, studies carried out in the past about the optical properties of tin dioxide showed that absorption region of SnO_2 films lies in the wavelength range as low as 250–300 nm, while in the VIS and NIR wavelength range it results to be transparent [11]. In the proposed sensor configuration, any effect able to modify the refractive index or the thickness of the sensing layer, or also the refractive index of the external medium would modify the fiber-film interface reflectance R_{123}, and thus the power level coming back from the fiber end [12]. When the target analyte is injected in the test ambient, the interaction between its molecules and the sensitive material leads to changes in the reflectance at the fiber-film interface and thus in the sensor output signal, as expected from (1).

III. Sensor Fabrication

A. ESP Deposition of SnO_2 Sensitive Layers

For the first time to our knowledge, SnO_2 sensitive overlays have been deposited upon the distal end of a standard SMF-28 optical fiber by means of the ESP technique by using an optimization and customization of the standard deposition technique. In fact, this method has been commonly used for the deposition of metal oxide (MOX) coatings on planar substrates [13]–[15]. The main principle of the method is the phenomenon of polarization of electrolyte (usually ethanol or water solutions of metal chlorides) on charged droplets by electrostatic field, applied between a vessel provided with a metal capillary and a heated substrate. The polarized droplets separate one from each other by means of repulsive forces and are carried by electrostatic field along its force lines [16]. The moving droplets form a cone in the space, called Tailor's cone [14]. The coverage of the substrate by droplets is quasi-uniform in terms of amount of drops per square unit. When droplets of solution reach the heated substrate (the temperature of the substrate is usually in the range 300 °C–450 °C), chemical reaction of metal chloride with water vapor of solution, stimulated by the temperature, takes place with formation of the oxide film [17]:

$$\text{MCl}_x + \frac{x}{2}\text{H}_2\text{O} \rightarrow \text{MO}_{\frac{x}{2}} + x\text{HCl}. \quad (3)$$

Thereby, MOX layer grows due to the thermal transformation of metal chloride to MOX as a consequence of the interaction with water vapor. All the deposition cycle usually is carried out in atmosphere with air pressures close to 10^5 Pa. The most important deposition parameters of the ESP are the metal chloride concentration, the precursor solution volume and the

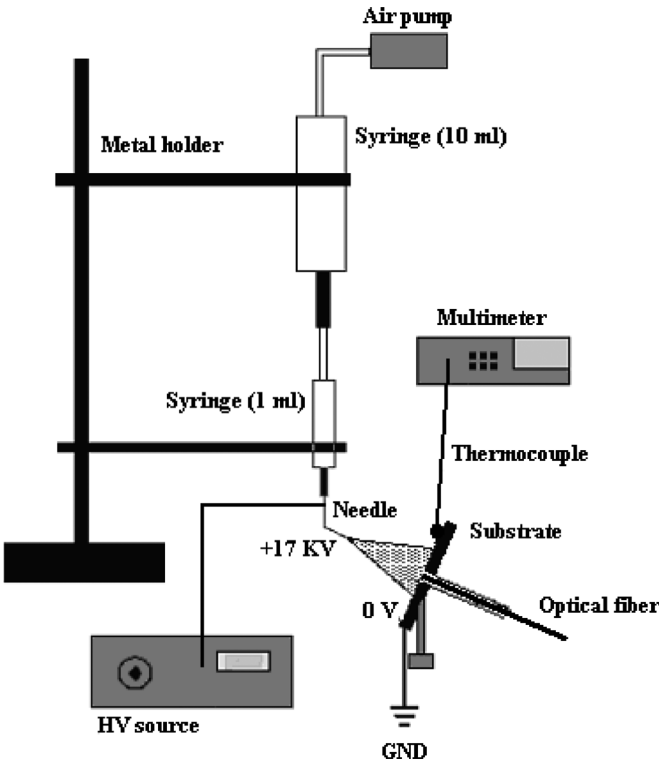


Fig. 2. Schematic view of the experimental setup used for the deposition of the sensitive layer onto the optical fibers.

substrate temperature [14]. It was shown that the concentration of the sprayed solution plays an important role in the morphology of the film. In particular, the higher concentration of the precursor, the higher the roughness of the film surface [14]. The substrate temperature during the deposition procedure determines structural properties of the layers like crystalline size and surface morphology and electrical properties like resistivity and charge carrier mobility. For the samples deposited at higher temperatures, low resistivity and higher roughness were observed, whereas for films deposited at temperatures less than 340 °C, high resistivity, lower crystalline size, and a lesser ratio of polycrystalline phase were found [18]. In light of this consideration, it is evident that the films properties can be tailored by varying the deposition parameters.

For the SnO_2-based chemical sensors fabrication, the optical fibers have been prepared by stripping the protective coating a few centimeters from the fiber end. The bare fiber has been washed in chloroform in order to remove any coating residuals. Then, the fiber end has been properly cut by using a precision cleaver in order to obtain a planar cross section, where the MOX films have been deposited. The deposition setup used for sensors fabrication is shown in Fig. 2. It consists of a high-voltage source (FUG, 0–30 kV), two syringes connected with a flexible pipe for the solution handling, a needle with an external diameter of 0.5 mm, connected with a high-voltage source $(17 \pm 0.1$ kV) in order to create a high electric field between the needle itself and a grounded metal substrate where the fiber end is located. The necessary temperature has been reached by means of a resistive heater, in contact with the substrate, constituted by two stainless steel plates of a few square centimeters and by a nichrome wire connected with a 300-W voltage source. The heater was supplied with a chromium-nickel thermocouple connected with a multimeter for the temperature monitoring. The distance between the needle and the optical fiber end was about 30 mm. The deposition has been performed at a constant temperature of 320 °C ± 5 °C. Liquid flow has been regulated by means of an air pump connected with the first syringe and kept constant to 0.37 ml/min. Tin dioxide films grew according to the following reaction [17]:

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl. \quad (4)$$

The SnO_2 films fabrication has been performed by means of 10 ml of an ethanol solution of $SnCl_4 \cdot 5H_2O$ with a concentration of 0.01 mol/l. During the deposition, it is also possible the formation of amorphous SnO phase. Thermal treatment is one of the ways to transform SnO_x to SnO_2 and clean the films surface from the other dopants like water or alcohol present in the initial solution [19]. For this reason, after the deposition procedure, the prepared samples have been annealed at 500 °C ± 5 °C for 1 h. The temperature has been increased from room temperature to 500 °C with a constant rate of 5 °C/min and, after the annealing procedure, the temperature has been decreased with the same rate down to the room temperature.

B. Spectral Characterization

In order to investigate the spectral properties of the deposited samples, a spectral characterization has been carried out in the VIS and NIR regions (400–1750 nm), by acquiring the transmittance spectra of the fabricated probes by means of a white light source (Ando AQ4303C) and an optical spectrum analyzer (Ando AQ6315A). To the aim, the white light source has been connected to the fiber coated by the sensitive layer, while a standard SMF-28 optical fiber, properly polished and cut, has been connected to the optical spectrum analyzer. The two fibers end faces have been brought in contact by using a precision positioning system in order to achieve the best fiber alignment. A high-resolution microscope has supported the operation allowing the fine alignment. The acquired transmittance spectra have been normalized to the white light source one, in order to obtain the films transmittance. Nevertheless, the acquired transmittance is not amplitude compensated, due to the fact that the source spectrum has been acquired by sending the power source directly to the optical spectrum analyzer. This means that the revealed transmittance takes into account also the optical losses due to the fiber ends alignment. However, these losses are not able to affect the wavelength behavior of the SnO_2 film transmittance spectrum, which, in turn, has been used in order to estimate the film thickness. In Fig. 3, we show the transmittance spectrum of a sample fabricated by using 10 ml of ethanol solution of $SnCl_4 \cdot 5H_2O$ with a concentration of 0.01 mol/l. The estimation of the film thickness has been carried out by considering the wavelengths at which the transmittance exhibits its maximum values, in accordance with the following expression [20]:

$$d = \frac{\lambda_1 \cdot \lambda_2}{2n_d(\lambda_2 - \lambda_1)} \quad (5)$$

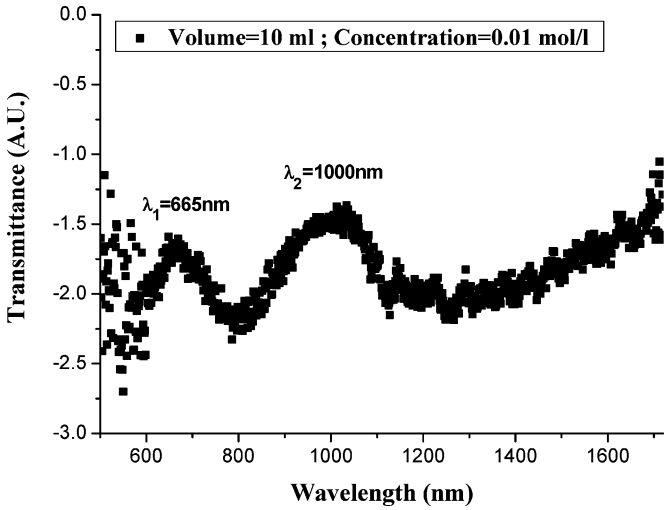


Fig. 3. Transmittance spectrum of the sensing probe fabricated with 10 ml of an ethanol solution of $SnCl_4 \cdot 5H_2O$ with a concentration of 0.01 mol/l.

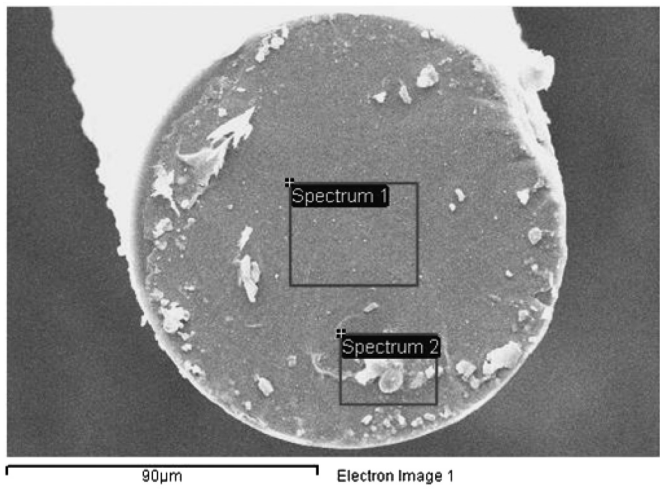
where d is the film thickness, n_d is the refractive index of the film, and λ_1 and λ_2 are the two wavelengths corresponding to two adjacent maxima. In (5), the refractive index of the tin dioxide overlayer has been assumed to be constant in the wavelength range 665–1000 nm and equal to 1.99 [21], [22]. This assumption means that the effect of the wavelength dispersion on n_d is not taken into account for the film thickness estimation. Nevertheless, the wavelength range is sufficiently narrow to lead to an acceptable error. The estimated value for the film thickness is approximately 500 nm.

C. Morphological Characterization

A morphological characterization of the deposited samples has also been carried out by means of SEM observations and EDS analysis. The latter one gives information about the precise elemental composition of the material under investigation. The SEM image of a SnO_2 film obtained by using the same deposition parameters of the one used for the chemical testing (10 ml of solution with a concentration of 0.01 mol/l) and the results obtained from the EDS analysis were reported in Fig. 4. It can be observed that a thin layer of SnO_2 covers the fiber surface and that few bigger agglomerates of carbon nature are also present upon it. This is attributed to the carbon present in the ethanol (C_2H_6O) used for preparing the precursor solution.

IV. Sensor Testing

A schematic view of the SOF sensor interrogation system is reported in Fig. 5. Reflectance measurements have been performed by lighting the optical fiber with a superluminescent light emitting diode operating at a wavelength of 1550 nm [23]. An optical isolator has been used in order to protect the power source by undesired light back-reflections. A 2×2 broadband coupler provides the appropriate connections between light source, sensing probe, and two receiving channels: one for the detection of the reflected signal and the other one for the source power monitoring, allowing the compensation of eventual source fluctuations. To enhance the signal to noise ratio and thus the system performances, synchronous detection



Spectrum	C	O	Si	Sn	Total
Spectrum 1		40.97	42.54	16.49	100.00
Spectrum 2	23.34	36.87	27.37	12.42	100.00

Fig. 4. SEM image and results obtained from the EDS analysis for a sensing probe fabricated with 10 ml of an ethanol solution of $SnCl_4 \cdot 5H_2O$ with a concentration of 0.01 mol/l.

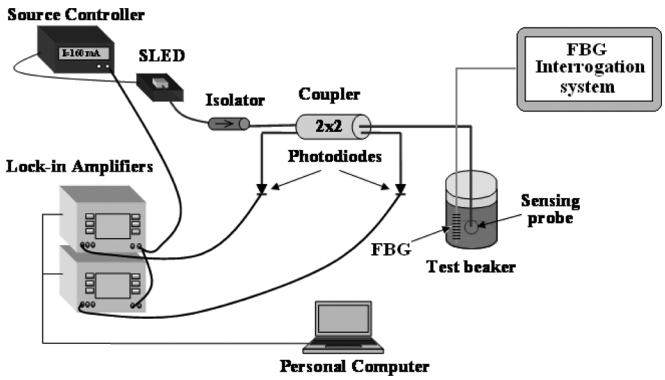


Fig. 5. Schematic view of the SOF sensor interrogation system for the detection of ammonia in water.

has been implemented. To the aim, the light source has been externally amplitude modulated at 300 Hz and the sensor outputs demodulated by means of two lock-in amplifiers. The normalized optoelectronic sensor output consists of the ratio between the signal reflected by the fiber coating and the one corresponding to the power emitted by the source [24]. In this configuration, any change in the sensor output can be attributed only to changes in the fiber-film interface reflectance R_{123} (1). The minimum detectable value, possible with the proposed interrogation system, is $6 \cdot 10^{-4}$. The sensing probe under test has been inserted in a beaker containing pure water. The addition of ammonia in the test environment has been managed by the accurate injection in the beaker of an aqueous solution of ammonia, whose volumes have been chosen in order to obtain the desired analyte concentrations. A magnetic stirrer has been used in order to stir the aqueous solution continuously and slowly for improving its homogeneity. In order to test

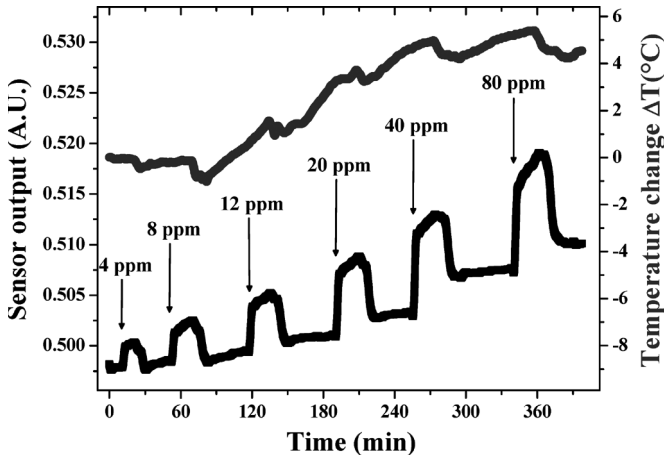


Fig. 6. Time response of the optical fiber-based sensing system to several injections of ammonia with concentrations in the range 4–80 ppm and temperature changes occurred inside the test ambient during the adsorption measurements.

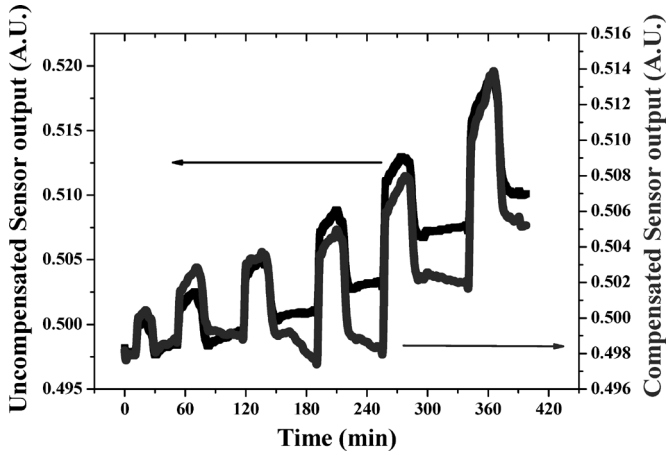


Fig. 7. Sensor response toward ammonia before and after the compensation of the undesired effects caused by the temperature changes occurred within the test chamber during the adsorption measurements.

the desorption capabilities of the proposed sensor, pure water has continuously been injected in the test beaker, while the contaminated water, previously present in it, is stilled out. In addition, in order to monitor the temperature changes occurring in the test ambient during the adsorption measurements, and to correlate them with drifts in the sensor response, a fiber Bragg grating (FBG) temperature sensor working at 1310 nm has also been inserted in the test beaker [25], [26].

V. Results

In order to test the performances of the proposed chemical sensor for ammonia detection in water environment, a tin dioxide thin film fabricated with 10 ml of an ethanol solution of $SnCl_4 \cdot 5H_2O$ with a concentration of 0.01 mol/l has been exposed to different concentrations of water ammonia. In Fig. 6, we show the transient response of the sensing system output when several injections of ammonia with different volumes were performed in the test beaker. The ammonia concentration range has been chosen to be 0–80 ppm by tailoring the volume of the analyte injected within the test ambient. The optoelectronic normalized signal and, thus, the reflectance, increases upon exposures as a consequence of the interaction between the ammonia molecules and the sensing overlayer. In addition, it can be seen that by increasing the ammonia concentration, higher reflectance change occurs.

Moreover, a change in the fiber-film reflectance, and thus in the output signal, would occur in case of changes of the external medium refractive index and thickness of the sensitive layer, as evident from (1). Nevertheless, because of the very low analyte concentrations, these effects can be assumed to be not relevant with respect to the whole sensor response. A significant drift in the baseline was also observed, to explain this effect on the sensor response, the thermal sensitivity was then analyzed.

In Fig. 6, the temperature variations occurred inside the test ambient during the experimental measurements are reported. In order to investigate the effect of these changes on the sensor response, a temperature compensation procedure has been carried out. It consists in the removal, from the sensor output

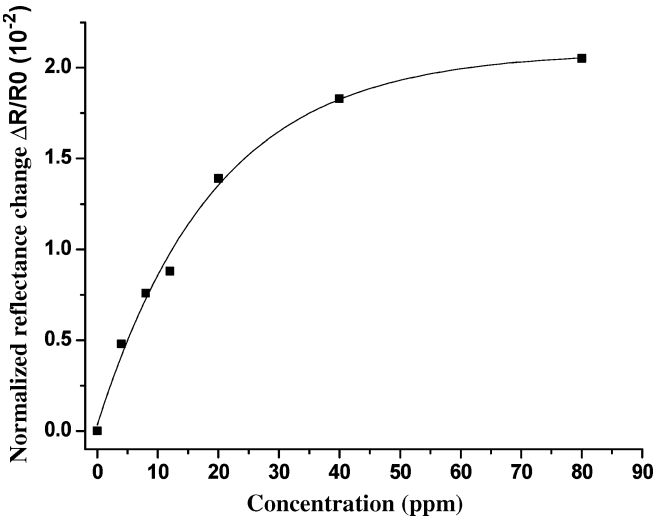


Fig. 8. Characteristic curve of the SOF sensor exposed to increasing concentrations of ammonia.

changes, of the variations induced by the temperature drift. To the aim, the tested sensor has been previously characterized against temperature, showing a sensitivity of approximately $2.1 \cdot 10^{-3}\ ^{\circ}C^{-1}$ (in terms of relative reflectance changes).

The sensor response before and after the compensation procedure is reported in Fig. 7. It can be clearly observed that for low analyte concentrations (4–20 ppm), the baseline drift was eliminated, demonstrating that thermal compensation is required in not temperature controlled environments.

In addition, it has been found that for higher concentrations of ammonia (40–80 ppm), the sensor does not completely recover the steady-state value. In addition, no changes in the relative reflectance change were observed between 40 and 80 ppm ammonia concentrations as shown in Fig. 8 where the sensitivity characteristics (in terms of relative reflectance changes) are reported. This could be attributed, in first analysis, to the saturation of the adsorption within the sensitive layer. Also, a different interaction mechanism (involving strongest bonds) could be involved in the case of high concentrations, however a deeper analysis is required to clearly identify the

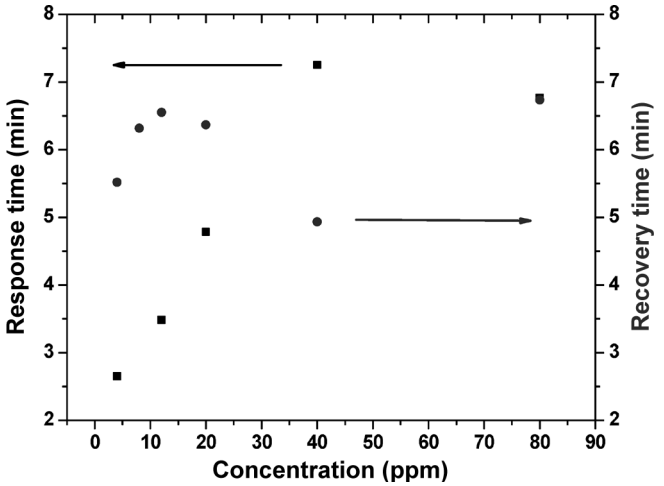


Fig. 9. Response and recovery times obtained by exposing the optical fiber probe to increasing concentrations of ammonia.

interaction mechanisms (physical and/or chemical sorption) at the basis of the low- and high-concentration responses.

From Fig. 8, it can be inferred that for low ammonia concentrations, sensitivity as high as $3 \cdot 10^{-4}$ ppm^{-1} has been obtained. Considering the minimum detectable value, possible with the exploited instrumentations, a resolution of approximately 2 ppm has been estimated. This value could be dramatically affected in case of strong temperature variations. For this reason, the monitoring of thermal drifts and the compensation of their effects on the sensors response are strictly required.

The response and recovery times of the tested sensor for each ammonia exposure is reported in Fig. 9. The response (recovery) time has been calculated by evaluating the time the sensor signal takes for passing from 10% to 90% (from 90% to 10%) of the whole signal shift occurring upon ammonia exposure (recovery). It can be seen that, except for the case of high ammonia concentrations (in correspondence of which the sensors is almost in saturation), the response time seems to be increasing with the analyte concentration, while the recovery time is quite constant. Based on the reported results, the proposed sensor exhibits very low response times, ranging approximately from 2 to 8 min, and recovery times of approximately 6 min.

VI. Discussion

In this section, a discussion about the possible sensitive layer-target molecules interaction mechanisms is presented. As well known in literature, optical, electrical, and structural properties of tin dioxide are connected and can influence each other [27]–[29]. Moreover, interaction of SnO_2 sensitive layer with adsorbed molecules strongly depends on the structure of the film [30]. In this paper, the experimental demonstration of the potentiality of the integration of this class of sensitive materials with the technology of optical fibers was carried out. In order to better understand the interaction mechanisms within the sensitive layer, a detailed investigation of the film structure should be carried out. However, here, different mechanisms of the sensor response dependently on the structure of SnO_2 coating have been proposed and some comments reported in order to consider the effects of the different interactions on the local optical properties of the sensitive layer. Two basic cases of SnO_2 film structures can be distinguished: porous and compact layers.

In case of porous layers, an immediate adsorption of ammonia molecules on open surface and their diffusion through pores toward optical fiber-tin oxide interface occur. Sensor response is ruled by the diffusion time and depends on the pore sizes. Another possible interaction mechanism could be the ammonia molecules chemisorption on grain boundaries with consequent diffusion within the interstitial sites between the SnO_2 grains.

In these mentioned cases, the interaction of the target molecules with the sensitive film should lead to the increasing of the average effective refractive index n_d and, in turn, to an increasing of the reflectance at the fiber-film interface, as expected from (1).

In case of compact layers, ammonia molecules simply adsorb on open surface of SnO_2 film. In this case, the bulk refractive index should not be interested in the ammonium sorption, while surface optical effects depending on the surface structure should occur. Ammonia chemisorption can lead to two main effects: charge transfer with increase of concentration of free electrons and formation of little-size space charge region at the surface, and thus a high electric tension forms in this region. Due to latter effect, high electric field appears on surface and diffusion of rich atoms of Sn or oxygen vacancies toward grain surface could be realized.

With regard to the selectivity of the proposed sensor, it is expected that a low specificity would be obtained. In fact, literature studies [31] have demonstrated a significant sensitivity of SnO_2 films toward different kinds of analytes. A detailed analysis on this aspect is actually in progress. Anyway, as with the case of modern electronic noses [32], a way to overcome this drawback could be the use of pattern recognition methods, such as principal component analysis and artificial neural network, applied on the responses of SOF sensors based on the same transducing principle but coated by different sensitive materials or also of sensors based on different principles of operations but coated by the same sensitive material. These methods are very often exploited by the researchers in order to improve the discriminating capabilities of unselective chemical sensors [33], [34]. Another way to improve sensor specificity would be the functionalization of the sensing surface, which should allow the sensors to respond only to a well-defined species and thus give straightforward information about its concentration inside the test environment [35].

VII. Conclusion

In summary, a SnO_2-based optical sensor for in water ammonia detection at room temperature has been proposed for the first time. The combination of the excellent sensing properties of SnO_2 films with the potentiality of the optical fiber technology has been proposed to develop a novel class of sensors that are able to work in water environment and at room temperature. Tin dioxide films have been successfully deposited onto the distal end of single-mode SOFs by means of the simple and low-cost ESP deposition technique. The films thicknesses of the deposited samples have been estimated by means of

spectral characterizations. The fabricated sensors have been employed in a refractometric system involving single wavelength reflectance measurements in order to test their sensing performances toward ammonia. A FBG temperature sensor has also been exploited in order to monitor the temperature changes occurring within the test ambient during the experimental measurements and for the compensation of the undesired effects that these variations could induce on the sensor response. The reported experimental results demonstrate the capability of the SOF sensor to detect ammonia in water at room temperature with a resolution of 2 ppm and response times of few minutes.

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