Optoelectronic sensor for ammonia detection in water based on SnO_2 films as sensitive layer

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Abstract

In this work, the possibility to detect ppm ammonia concentrations in water environment, at room temperature, by means of Standard Optical Fibers (SOFs) sensors coated by Metal Oxides (MOXs) films has been demonstrated. Electro-spray pyrolisis technique has been used to deposit SnO_2 films onto the distal end of single-mode optical fibers. The sensor operating principle relies on the measurement of the light intensity reflected by the fiber-sensitive layer interface: the pollutant molecules adsorption within the MOX film causes a change in its complex dielectric function and thus in the fiber-film reflectance. Spectral characterization of the obtained sensing probes has been carried out in the range 400-1750nm. Single wavelength reflectance measurements have been carried out to test the sensor performances for ppm ammonia detection. High sensitivity to the target analyte, response times of approximately 10-20 minutes and a Limit Of Detection as low as sub-ppm has been observed.

Keywords: Optical fiber sensors, tin-dioxide film, ammonia detection in water

1 Introduction

In the last years, the use of optical fiber sensors has expanded rapidly. The use of an optical sensing mechanism offers several advantages like the immunity to electromagnetic interference and the dual functionality to serve as transducers and sensing data transportation systems. In this paper, tin dioxide films have been integrated with optical fiber technology in order to develop optoelectronic sensors able to work in water environment for ppm detection of ammonia at room temperature [1]. Electrostatic spray pyrolisis technique has been used for Metal Oxide (MOX) film deposition [2]. Spectral characterization of the obtained sensing probes has been carried out in the range 400-1750nm. Single wavelength reflectance measurements have been carried out to test the sensing performances. Experimental results are here presented.

2 Methodology

2.1 Principle of operation

With reference to fig. 1, the principle of operation relies on the deposition of a film of tin dioxide on the distal end of a standard single mode fiber. In this situation, the reflectance at the fiber end interface can be expressed as function of the optical and geometric features according to:

$$R = f\left(\varepsilon_{eff}, \lambda, \varepsilon, d, \varepsilon_{ext}\right) \quad (1)$$

where ε_{eff} is the effective dielectric constant of the guided mode, λ is the optical wavelength, d is the film thickness, ε_{ext} is the external medium dielectric constant and $\varepsilon = \varepsilon_1 + j\varepsilon_2$ is the complex dielectric function of the SnO_2 film. Any effect able to modify the real or the imaginary part of the sensing layer dielectric function would modify the film reflectance according to the following equation:

$$\Delta R = \frac{\partial R}{\partial \varepsilon_1}\Delta\varepsilon_1 + \frac{\partial R}{\partial \varepsilon_2}\Delta\varepsilon_2 \quad (2)$$

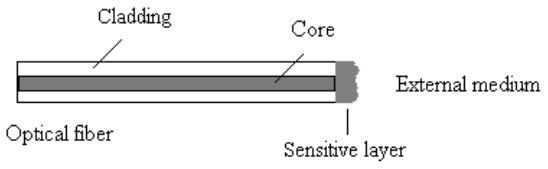


Figure 1. Schematic view of the sensing probe

2.2 Sensors fabrication

The sensors have been fabricated by coating the distal end of single mode SOFs with tin dioxide layer. The

electrostatic spray pyrolisis technique has been used to deposit the SnO_2 films. The sensing probes have been previously prepared by stripping the fiber protective coating a few centimeters from the fiber end. The bare fibers have been washed in chloroform in order to remove any coating residuals. Then the fibers end have been properly cut by using a precision cleaver in order to obtain a planar cross-section, where the MOX film has been deposited. The principle of electrostatic spray pyrolisis relies on the spraying of an initial liquid solution from a capillary to a substrate heated at a temperature ranging between 300 to 450°C, by means of an applied electrical field between them. Electrostatic spray pyrolisis allows to change the 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 [2]. It was shown that the concentration of the sprayed solution plays an important role in the morphology of the film. The higher concentration of the precursor was used, the higher roughness of the surface was observed. The substrate temperature during the deposition determines structural properties of the films 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 was observed whereas for films deposited at temperatures less than 340°C high resistivity, lower crystalline size and less ratio of polycrystalline phase were found [3]. For SnO_2 films fabrication different volumes (ranging from 1 up to 10 ml) of an ethanol solution of $SnCl_4 \cdot 5H_2O$ with different concentrations (ranging from 0.01 up to 0.1 mol/l) have been prepared.

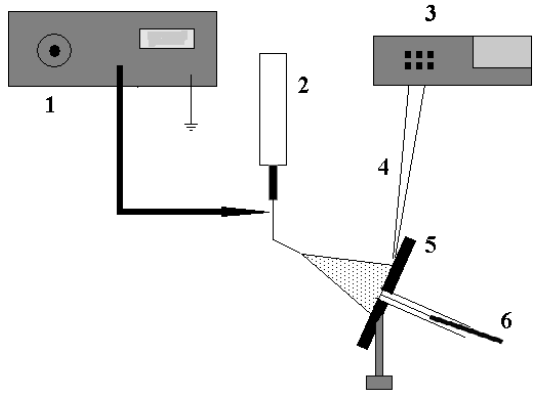


Figure 2 Deposition setup: high voltage source (1), vessel with solution (2), multimeter (3), thermocouple (4), heater (5), SOF (6)

The deposition set-up used for sensors fabrication is shown in Fig. 2. It consists of a plastic vessel with the ethanol solution, a high voltage source, a needle with a diameter of 0,5 mm and a resistive heater. The pressure over solution has been kept constant with air pump connected with the vessel and the solution flow has been 0.37 ml/min. Before the deposition step, the optical fiber has been inserted in a quartz thin tube previously integrated within the heater. The depositions have been performed at a constant temperature of 320°C in order to get a good compromise between a small crystalline size and an high ratio of polycrystalline phase. The applied voltage has been 17 ± 0.1 kV and the distance between the needle and the fiber tip has been about 30mm. The MOX layer growths due to the thermal transformation of metal chloride to metal oxide as a consequence of the interaction with water vapor according to the following reaction [4]:

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl \quad (3)$$

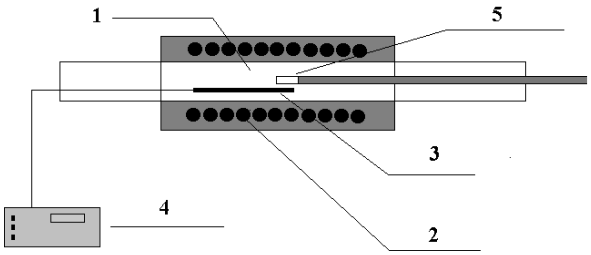


Figure 3 Annealing setup: quartz pipe (1), nichrom wire (2), thermocouple (3), voltage source (4) and sensing probe (5)

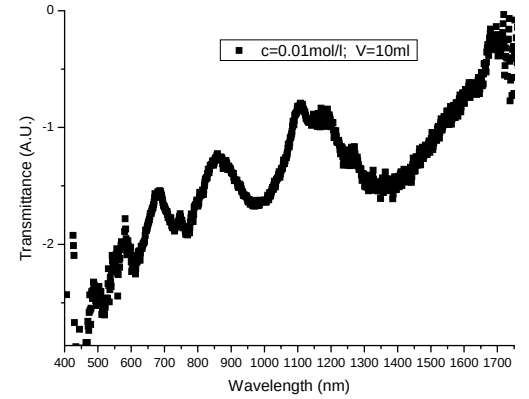
During the deposition, it is also possible the formation of amorphous SnO phase. Thermal treatment is one of the ways to transform SnO_x to SnO_2 and clean the films surface from the other dopants like water or alcohol existed in the initial solution [5]. After deposition the obtained samples have been annealed at 500°C for 1 hour. The setup used for the annealing is shown in figure 3. The optical fibers with the sensitive layer have been inserted in a quartz pipe with a diameter of 20mm and a length of 300 mm. The heating element was constituted by two stainless steel plates of a few square centimetres and by a nichrom wire connected with a 300W voltage source. A thermocouple connected to a multimeter allowed to monitor the annealing temperature. The SOFs have been settled up with a holder into the pipe. The temperature has been increased from room temperature to 500°C with a constant rate of 5°C/min. Then temperature has been decreased with the same rate to room temperature.

3 Experimentals

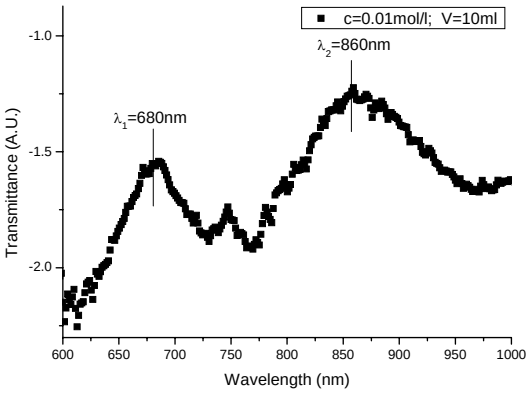
3.1 Characterization

In order to investigate the spectral properties of the deposited films, the transmittance of the films deposited has been measured. It is well known that tin oxide is wide band gap material with E_g=3,6eV. The past studies of the optical properties of tin-dioxide

have showed that absorption region of tin oxide film lays in short wavelength region 250-300nm, while in visible and IR wavelength regions the tin-dioxide is transparent (Transmittance 85-90 %) [6].



(a)



(b)

Figure 4 Transmittance spectrum of a sensor realized with a volume of 10ml of ethanol solution with a concentration of 0.01mol/l. (a) Interference fringes used for thickness estimation (b)

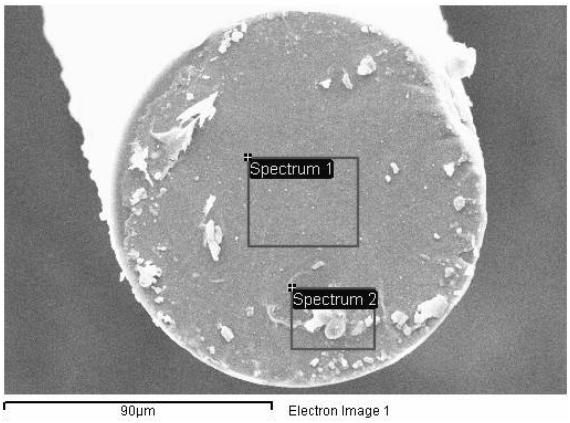


Figure 5 SEM image of tin dioxide film onto SOF

In order to get a spectral characterization of the deposited films in the visible and NIR region, a white light source (Ando AQ 4303C) and an optical spectrum analyzer (Ando AQ6315A) have been used. The white light source in the range 400-1800nm has been connected to the fiber coated with the SnO_2 film, on the other side a SMF-28 has been connected to the optical spectrum analyzer (350-1750nm). Here the fiber end has been properly cut by using a precision cleaver in order to obtain a planar cross-section. The two fiber end faces have been brought in contact one with each other by using a precision positioning system with nanometric resolution in order to achieve the best alignment. A microscope has supported the operation allowing the fine alignment. The recorded transmitted spectra have been normalized respect to the white light source spectrum in order to get the transmittances of the films. The acquisition of the source spectrum has been performed at the source emission. This means that the revealed transmittance takes into account also the optical losses along the optical chain. However, these losses are not able to affect the shape of the transmittance spectrum., which, in turn, was used in order to estimate the film thickness.

In figure 4 (a) has been shown the transmittance spectrum of a sample realized with a volume, *Vol*, of 10ml of ethanol solution and with a concentration, *c*, of 0.01mol/l. In the wavelength range 600-1400nm interference fringes have been manifested. The first two maxima of the interference fringes, showed in figure 4 (b), have been used to determine the thickness of the films fabricated, assuming that refractive index is constant in the corresponding spectral region. Investigations of refractive index n of tin oxide films in dependence on wavelength showed that in the region of λ=300-1000 nm *n* decreases if λ increases changing from 2,6 to 1,96. In order to estimate the film thickness a refractive index of 1.99 has been supposed [7-8] Film thickness can thus be calculated using the expression [9]:

$$d = \frac{\lambda_1 \cdot \lambda_2}{2n(\lambda_2 - \lambda_1)} \qquad (4)$$

where d is the film thickness, n is the refractive index of the film and λ_1 and λ_2 are the two wavelengths corresponding to the consecutive maxima used for thickness estimation. Numerical values for these latter are respectively 680nm and 860nm as shown in figure 4 (b). The two adjacent fringes used for thickness estimation revealed a film thickness of about 816nm.

Microstructural characterization has been also carried out by scanning electron microscopy (SEM) and the SEM image has been shown in figure 5 for a sensor fabricated with the same deposition parameters (Vol=10ml and c=0.01mol/l).

3.2 Experimental setup

A schematic view of the optical fiber based sensing system [10] has been reported in Fig. 6. Reflectance measurements have been performed by lighting the optical fiber with a superluminescent diode (40nm

bandwidth) operating at a wavelength of 1550nm. An optical isolator has been used in order to protect the source by undesired light back-reflections. A 2x2 in-fiber coupler provides the appropriate connections between light source, sensing probe and two receiving channels: one for the reflected signal detection and another one for the power monitoring, allowing the compensation of eventual source fluctuations. To enhance the system performances, synchronous detection has been implemented: the light source has been externally amplitude modulated at 300Hz and the sensor outputs have been recovered by two lock-in amplifiers. The normalized optoelectronic sensor output, V, consists of the ratio between the reflected signal from the sensing probe and the one corresponding to the power emitted by the source. In this configuration any change of the system output signal can be attributed only to changes in the film reflectance. With the actual set-up, a minimum detectable output ΔV_{min} of $6 \cdot 10^{-4}$ is possible.

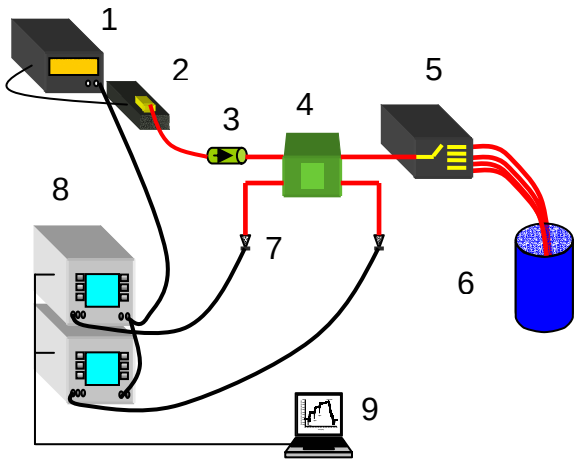


Figure 6 Schematic views of the optical fiber based sensing system, composed by source controller (1), laser (2), isolator (3), coupler (4), opt. switch (5), sensors within test beaker (6), photodiodes (7), lock-in amplifiers (8), PC and DAQ system (9)

In order to test simultaneously more than one sensor, an optical switch 1x4 has been provided. For each exposition three sensors and one optical fiber without film have been tested. The last one has been inserted in order to distinguish empirically the effect of the external medium refractive index changes from the effect of physical adsorption of the analyte. A switching time of two seconds has been set. The sensing probes under test have been previously bonded to a stable arm and then dipped in a beaker filled with pure water. A magnetic stirrer has been used in order to continuously and slowly stir the aqueous solution. The equilibrium of the films with the pure water has been expected. Pollutant has been mixed with pure water in a different beaker. The volume of the ammonia solution has been chosen in order to get the desired ppm concentration of ammonia in the test beaker. After the achievement of a stable base line of the sensor output, the prepared ammonia solution has been added to the test beaker by using a Teflon pipe connecting the two beaker. The flux has been simply controlled by a tap. To provide desorption of ammonia from the film, a pure water flux has been injected in the test beaker and a reservoir has been provided in order to collect the excess water outcoming from the test beaker. The necessary connections have been provided using Teflon pipes and taps.

The temperature has been constantly monitored by a fiber Bragg grating inserted in the beaker [11-12] working at 1310nm.

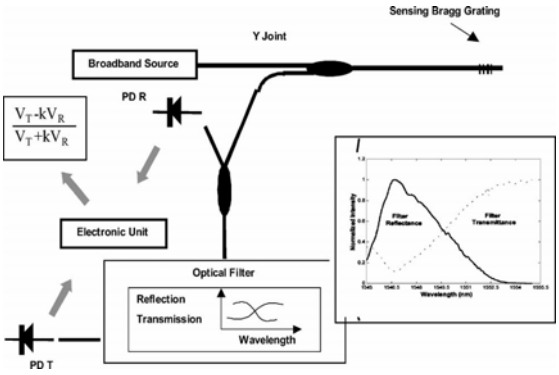


Figure 7 Schematic view of the fiber Bragg grating sensing system

The Bragg temperature sensor interrogation system has been shown in figure 7. A super-luminescent diode operating at 1310nm with a max power level of 2mW and 40nm bandwidth has been used. The linear filter based on grating technology has been designed to exhibit a transmission and reflection response linearly varying in the range 1305-1315nm (10nm linear range). The slope of the optical filter in transmission directly calculated as the rise in percent over the run in nanometres, is of approximately of 7%/nm. This slope is valid between about the 10–90% of the range. The functions of the electronic unit are the collection and the elaboration of the received signals, an A/D converter (16 bit 330 kHz bandwidth) is responsible for the digitalization of the received signals. Two transimpedance amplifiers with unitary gain and low noise has been used at the output of the two photodetectors. Low pass filters has been used in order to reduce the noise.
A proper DAQ system has been implemented for data storage and manipulation in LabView software ambient.

4 Results

In order to evaluate the MOX based optical sensors response to ppm concentrations of ammonia, several insertions in the test beaker of an ammonia aqueous solution (20.5% in wt.) have been performed. In fig. 8

the optical response to four different expositions to ammonia of the tin dioxide based sensor with thickness of 816nm and prepared with Vol=10ml and c=0.01mol/l has been shown. The concentrations of NH_4OH in the aqueous solution of the test beaker has been calculated to be respectively 4, 4, 8 and 12ppm.

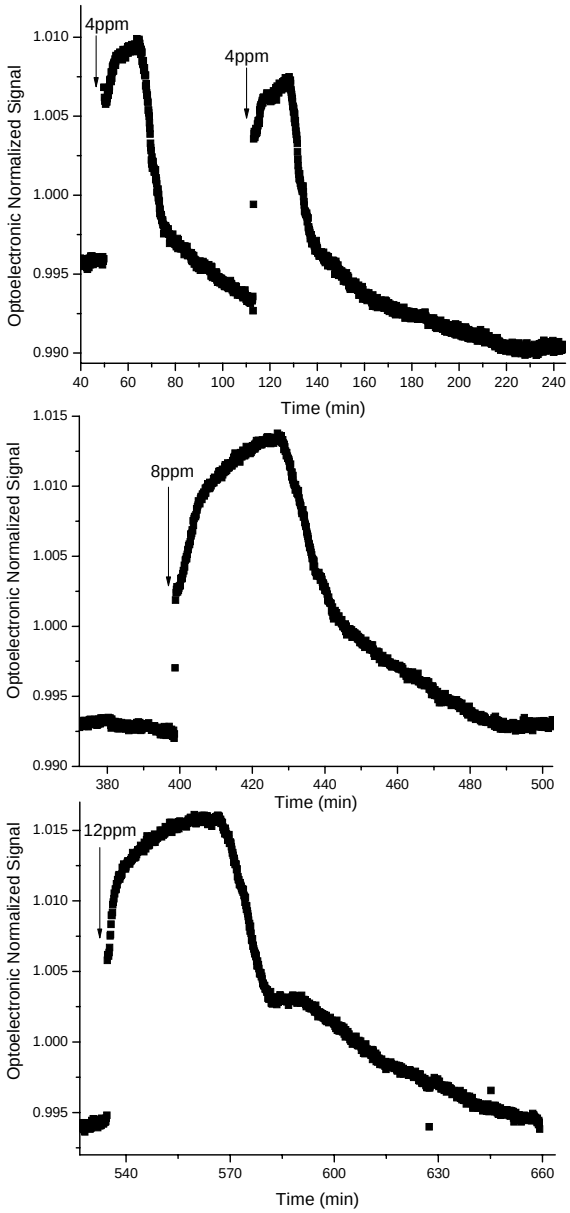


Figure 8 Time response of the silica optical fiber sensor coated with a tin dioxide film to ammonia

The optoelectronic normalized signal, directly related to the film reflectance, increases upon ammonia exposition. The initial variation of the sensor output has not been appreciated because has been faster then the sampling time (1 Sample every 8 seconds). For low concentrations of ammonia, the water refractive index changes can be neglected in respect to the variations in the dielectric function of the film due to the analyte sorption. In fact, negligible variations have been observed in a SOF without tin-dioxide overlay added in the same test beaker.

Similar responses have been revealed by the sensor when equal concentrations of ammonia have been inserted in the test beaker. In the first graph in figure 8 has been shown the time response of the sensor consequent to two 4ppm ammonia additions. The optoelectronic signal variations recorded have been respectively $1.36 \cdot 10^{-2}$ and $1.38 \cdot 10^{-2}$. It is worth to note that the difference is less than the system resolution.

The response times observed have been estimated to be of approx. ten, ten, twenty and twenty-five minutes, respectively, for the four ammonia additions. Longer recovery times have been observed ranging from thirty minutes up to one hour.

In fig. 9 the sensitivity curve is reported in terms of relative reflectance changes. A non-linear dependency of the optoelectronic normalized signal on the ammonia concentration has been revealed demonstrating an increase of approximately 2.3% for an overall ammonia concentration of 12ppm and a maximum working range of about 10ppm. Considering the minimum detectable normalized signal, a limit of detection of 0.6ppm has been obtained.

A variation maximum of 4°C has been recorded during the analyte sorption and recovery steps. The sensitivity of the tin-dioxide sensor output to temperature changes has been measured for the fabricated films. A sensitivity of about $4 \cdot 10^{-4} °C^{-1}$ has been revealed by the tested film with thickness of 816nm. Therefore, temperature changes are able to affect the sensor capability to detect low ammonia concentrations, because a few degree temperature variation leads to variations in the third decimal digit of the normalized optoelectronic signal. In order to avoid the degradation of the system performances, it is useful to compensate the temperature effect on the sensor output. To this aim, the fiber Bragg grating technology can be integrated with the refractometric system.

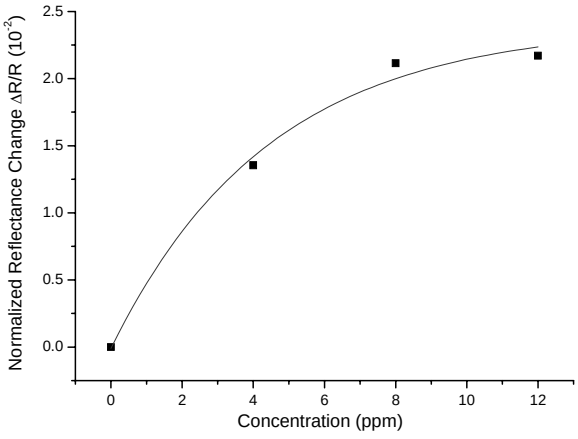


Figure 9 Normalized reflectance changes over concentration unit

A fiber optic sensing system for multiparameter sensing can be implemented [13], by splicing the optical fiber including the fiber Bragg grating with the ammonia sensing probe. A wavelength division multiplexing coupler has to be used in reception for the discrimination between the refractometric signal (1550nm) and the Bragg signal (1310nm) working in different spectral regions.

5 Conclusions

In summary, a SnO_2 based optical sensor for in water ammonia detection at room temperature has been demonstrated. The combination of the excellent sensing properties of MOX films with the potentiality of the optical fiber technology was proposed to develop a novel class of sensors able to work in water and at room temperature. Tin dioxide films have been successfully deposited onto the distal end of single-mode SOFs by means of the electrostatic spray pyrolisis deposition technique. The films thickness has been estimated from interference fringes. The fabricated sensors have been employed in a reflectometric system involving single wavelength reflectance measurements in order to test the sensing performances. Here, experimental results are reported on the sensor capability to detect ppm ammonia concentrations in water at room temperature. Fast time response in the minutes range and sub ppm resolution has been demonstrated.

6 Acknowledgements

The authors wish to thank Manlio Colella (Laboratorio di Microscopia Ottica di Ingegneria, Università Federico II, Napoli) for the SEM analisys

7 References

1. M. Pisco, M. Consales, R. Viter, V. Smyntyna, S. Campopiano, M. Giordano, A. Cusano, A. Cutolo, "Novel SnO_2 based optical sensor for detecting the low ammonia concentration in water at room temperatures", International Scientific Journal Semiconductor Physics, Quantum Electronics and Optoelectronics, Vol.8, 2005
2. El Hadj Aldaphe Diagne, M. Lumbreras, "Elaboration and characterization of tin oxide - lanthanum oxide mixed layers prepared by electrostatic spray pyrolisis technique", Sensors and Actuators, B 78 (2001) 98-105
3. P.S. Patil, R.K. Kawar, T. Seth, D.P. Amalnerkar, P.S. Chigare, "Effect of substrate temperature on structural, electrical and optical properties of sprayed tin dioxide (SnO_2) thin films", Ceramics International, Vol. 20 (2003) pp. 725-734
4. G.S. Korotchenkov, S.V. Dmitriev, V.I. Brynzari, "Processes development for low cost and low power SnO_2 thin film gas sensors (TFGS)", Sensors and Actuators B 54 (1999) 202–209
5. R. Ramamoorthy, M. K. Kennedy, H. Nienhaus, A. Lorke, F. E. Kruis and H. Fissan, Surface oxidation of monodisperse SnO_x nanoparticles, Sensors and Actuators B: Chemical Volume 88, Issue 3 , 10 February 2003, pp.281-285.
6. Garima Jain, R. Kumar, "Electrical and optical properties of tin oxide and antimony doped tin oxide films", Optical Materials 26 (2004) 27–31.
7. González-Leal, J.M.; Prieto-Alcón, R.; Stuchlik, M.; Vlcek, M.; Elliott, S.R.; et. al., "Determination of the surface roughness and refractive index of amorphous $As_{40}S_{60}$ films deposited by spin coating", Optical Materials, 27, 2, (2004) pp. 147-154
8. Losurdo, M.; Barreca, D.; Capezzuto, P.; Bruno, G.; Tondello, E., "Interrelation between nanostructure and optical properties of oxide thin films by spectroscopic ellipsometry ", Surface and Coatings Technology, 151-152,(2002) pp. 2-8
9. J. C. Manifacier, J. Gasiot, J.P Fillard, "A simple method for the determination of the optical constants n, k and the thickness of a weakly absorbing thin film", J. of Physics E :Scientific Instruments, Vol. 9, 1002-1004 1976
10. A. Cusano, A. Cutolo, M. Giordano, and L. Nicolais, "Optoelectronic refractive index measurements: application to smart processing," IEEE Sensors J., vol. 3, pp. 781-787, December 2003.
11. A. Cusano, G. Breglio, M. Giordano, L. Nicolais, A. Cutolo, "Multifunction Fiber Optic Sensing System for Smart Applications", IEEE/ASME Trans. mechatronics, 9, 1, Mar 2004
12. A. Cusano A. Cutolo, M. Giordano, A. Calabrò, "Dynamic strain measurements by fibre Bragg grating sensor", Sensors and Actuators A, 110(1-3), 2003, pp276-281.
13. Cusano, A.; Persiano, G.V.; Russo, M.; Giordano, M., "Novel optoelectronic sensing system for thin polymer films glass transition investigation", Sensors Journal, IEEE, 4, Issue 6, Dec. 2004 pp837 - 844