*Semiconductor Physics, Quantum Electronics & Optoelectronics, 2005. V. 8, N 1. P. 95-99.*

PACS: 07.07.Df, 42.79.Pw

# Novel $SnO_2$ based optical sensor for detection of low ammonia concentrations in water at room temperatures

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**Abstract.** In the work, presented are preliminary experimental results on the capability of a metal oxide (MO) based optical sensor to perform ammonia detection in water environment at room temperature. The electro-spray pyrolysis technique was used to deposit $SnO_2$ films on the distant end of standard silica optical fiber (SOF). Reflection spectra of the studied samples were preliminarily characterized in the range of 1520 to 1620 nm by using a tunable laser and an optical spectrum analyzer. Single wavelength reflectance measurements were carried out to test the sensing performances for detecting the ammonia of concentration from 4 to 20 ppm. High sensitivity to the target analyte and fast response times were observed. From the results obtained, the detection limit close to a sub-ppm level was achieved.

**Keywords:** optical fiber sensor, tin dioxide film, ammonia detection.

Manuscript received 09.02.05; accepted for publication 18.05.05.

## 1. Introduction

Over the past decade, applications of optical fiber sensors expanded rapidly. The main advantages related to the use of optoelectronic sensing devices that are resistent to electromagnetic interference and possess dual functionalities due to their capability to serve as transducers and sensing data communication systems. Sensitive properties of tin-dioxide thin films to different chemical compounds were studied by many authors. A lot of different types of resistive tin-dioxide sensors were performed for detecting hydrogen, carbon monoxide, methane, ammonia, nitrogen oxides, and different organic solvents [1]. All of these sensors operate being based on the principle of a resistance change with regard to gas adsorption on their surfaces. Because of it, they have never been used for detection, contaminations in liquid. Furthermore, the gas sensitivity of MO based sensors usually reaches a peak at the high temperatures (250 to 450 °C). Adding catalytic dopants (Pt, Pd, Au, and Ag) makes it possible to decrease an operating temperature but didn't minimize strongly the heater consumption power [2]. To our knowledge, there are no tin dioxide sensors operating in liquids at room temperatures. Here, for the first time, tin-dioxide thin films were integrated with the optical fiber technology in order to develop a new class of optoelectronic sensors suitable to be used for ppm chemical detection in water medium at room temperatures. The electrostatic spray pyrolysis technique was used for MO film deposition [3]. Its process parameters can be appropriately adapted to obtain the films with different thicknesses and surface structures. Spectral characteristics of the obtained sensing probes were determined from 1520 to 1620 nm. The single-wavelength (1550 nm) film reflectance was measured to test the sensing performances of the realized sensors. Experimental results on the capability to perform the ammonia detection with ppm resolution at room temperature are presented in this paper.

## 2. Experimental

### *2.1. The principle of optical sensor operation*

The main disadvantages of resistive MO sensors are high operating temperatures and a drift of baseline on expose to external factors. Besides, these sensors are useless for liquid detection because of the short circuit between electrodes. Integration of MO technologies with optoelectronic measuring systems allowed us to solve some of the above problems.

As seen from Fig. 1, the main part of the sensor is the thin film of tin dioxide deposited on the distant end of a

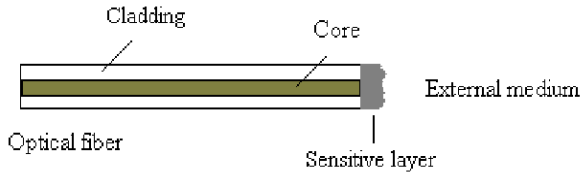


**Fig. 1.** Schematic view of SOF probe.

standard single-mode fiber. The operating principle is based on measurements of the power reflected from the tin-oxide film – external medium interface. In this situation, the reflectance at the fiber end interface can be expressed as a function of the optical and geometric parameters in accord with

$$R = f\left(n_{\text{eff}}, \lambda, \varepsilon, d, n_{\text{ext}}\right) \qquad (1)$$

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

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

*2.2. Sample preparation*

The electrostatic spray pyrolysis method allows us to change the deposition conditions in a wide range. The most important deposition parameters are the metal chloride concentration, solution volume, and substrate temperature. They strongly influence on the structural properties of the film such as crystallite size, thickness, and porosity. It means that the film structure can be controlled by varying the deposition parameters. The principle of electrostatic spray pyrolysis is based on spraying an initial liquid solution from a capillary onto a substrate heated to the temperatures of 300 to 450 °C, by means of an applied electrical field between them. The MO layer grows due to the thermally enhanced transformation of metal chloride into metal oxide due to interaction with water vapour. The sensing probes were prepared by stripping the fiber protective coating of a few centimetres from the fiber end. The bare fiber was washed with chloroform to remove any coating residuals. Then, the fiber end was cut using a precision cleaver in order to obtain a planar cross-section where the MO films were deposited. For $SnO_2$ film fabrication, two different volumes (4 and 10 ml) of the ethanol solution of $SnCl_4 \cdot 5H_2O$ with three different concentrations (0.01, 0.05, and 0.1 mol/l) were prepared. Using these deposition parameters, few-micron MO based films were obtained. The deposition setup used

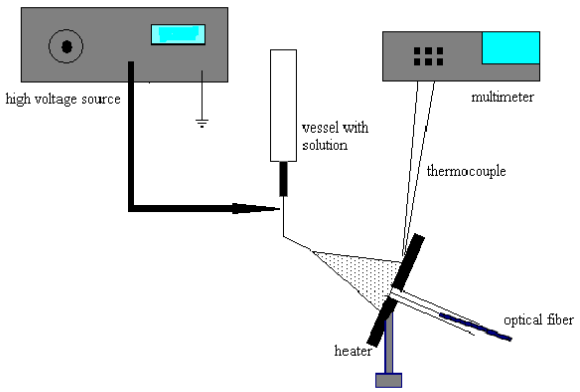


**Fig. 2.** Deposition setup.

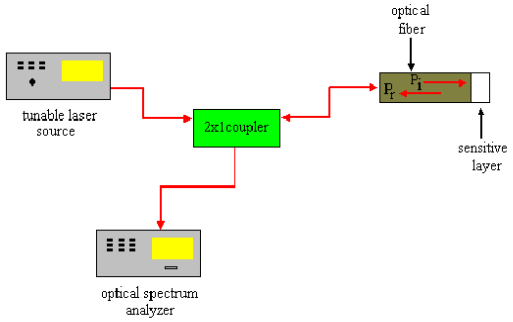


**Fig. 3.** Characterization setup.

for sensors fabrication is shown in Fig. 2. It consists of a plastic vessel with the ethanol solution, a high voltage source (FUG, 0–30 kV), a needle with the diameter of 0.5 mm, and a resistive heater. Before the deposition stage, the optical fiber was inserted into a thin quartz tube previously integrated within the heater. The deposition was performed at the constant temperature 300 °C. The applied voltage was $17 \pm 0.1$ kV. The distance between the needle and fiber tip was about 30 mm. The tin-dioxide film was formed according to the following reaction [4]:

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

Structural properties of deposited films were investigated using SEM methods.

*2.3. System characteristics and sensor testing*

For investigating the optical properties of $SnO_2$ films, the reflectance of fabricated films was measured in the wavelength range of 1520 to 1620 nm with using a tunable laser (Ando AQ4321D) and an optical spectrum analyzer (Ando AQ6317 C). The setup is shown in

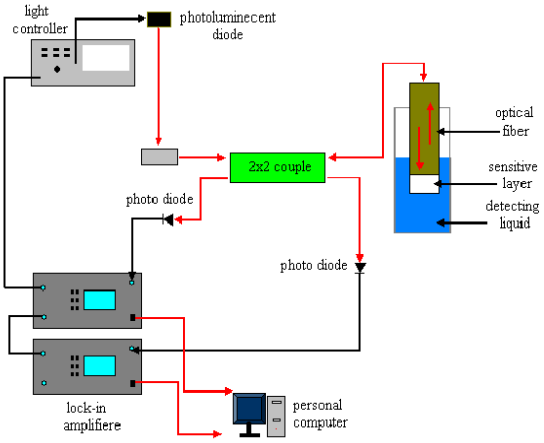


**Fig. 4.** Schematic view of the optical fiber based sensing system.

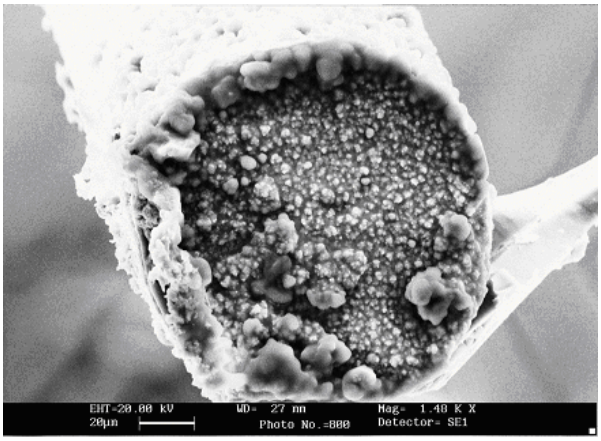


**Fig. 5.** SEM image of tin dioxide film onto SOF.

Fig. 3. A 2×1 in-fiber coupler was used to provide the appropriate connections between the tunable laser, sensing probe, and spectrum analyzer.

A schematic view of the optical fiber based sensing system is demonstrated in Fig. 4 [5]. Reflectance measurements were performed by illumination of the optical fiber with a superluminescent diode (40 nm bandwidth) operating at the wavelength 1550 nm. An optical isolator was used to protect the source from undesired light back-reflections. A 2×2 in-fiber coupler provided the appropriate connections between the 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 was implemented: the intensity magnitude of the light source was 200-Hz modulated, and the sensor output signal was recovered by two lock-in amplifiers. The normalized optoelectronic sensor signal $V$ consists of the ratio between the reflected signal from the sensing probe and that corresponding to the power emitted by the source. In this configuration, any change of the system output

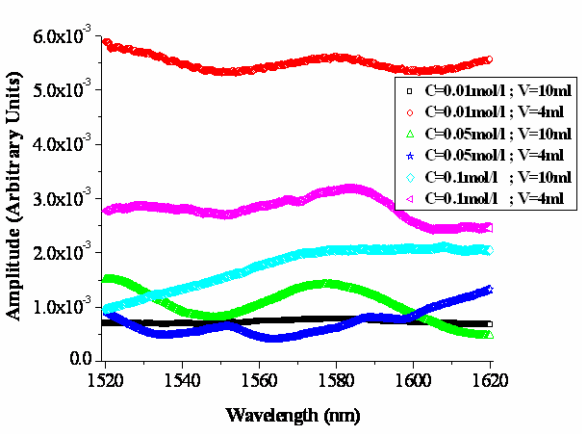


**Fig. 6.** Reflectance spectra of the tin-dioxide films.

signal can be attributed only to changes in the film reflectance. With the actual setup, a minimum detectable output $\Delta V_{min}$ of $10^{-4}$ is possible. The sensing probes have been previously bonded to a stable arm and then dipped in a vessel filled with 500 ml of pure water. A magnetic stirrer was used in order to continuously and slowly mix the aqueous solution, the temperature of which was all the time monitored by a thermocouple inserted within the vessel. A proper DAQ system was implemented for data storage and processing.

For evaluating the MO based optical sensor response to the ppm concentrations of ammonia, several inclusions into the test vessel of the ammonia aqueous solution (20.5 wt. %) were performed using a precision micropipette (Gilson). The target analyte quantity present in the aqueous solution for each inclusion was calculated to be approximately 4 ppm. In these conditions, the water refractive index is very weakly influenced, and its effect can be neglected in respect to the changes in the optical properties of the film due to the analyte sorption. Thus, we obtain the optical response of our tin dioxide based sensor fabricated using $SnCl_4$ concentration (0.1 mol / l) and a solution volume 10 ml in 3-µm film for five cases of ammonia concentrations was obtained. The film temperature was kept constant at 20 °C by inserting the fiber end in a thermostat.

## 3. Results and discussion

Fig. 5 shows the SEM image of a tin-dioxide film. The surface appears rough because of presence of $SnO_2$ grains. This $SnO_2$ distribution generally enhances the analyte molecules adsorption within the film due to increasing the surface area responsible of the film sorption. The obtained spectrum is shown in Fig. 6. As can be seen, different deposition parameters lead to different reflectance spectra, demonstrating the optical and geometric parameters dependence of the fabricated

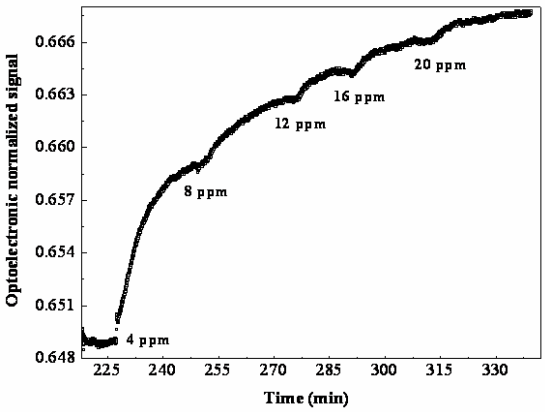


**Fig. 7.** Time response of the silica optical fiber sensor coated with a tin dioxide film to ammonia.

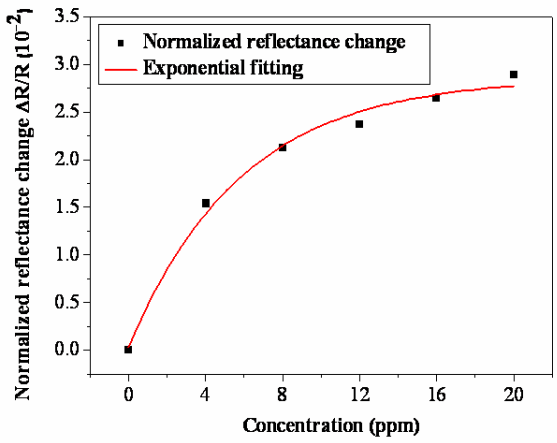


**Fig. 8.** Normalized reflectance changes over concentration unit.

films on the solution volume and $SnCl_4$ concentration. Very low reflectance values have been observed from these measurements. This could be attributed to two effects: the light absorption inside the films or light scattering at the film – external medium interface due to the surface roughness. However, it was shown in [6] that the absorption coefficient of tin-dioxide films equalled to 0.18…0.22 in the wavelength range of 1520 to 1620 nm. Therefore, a low reflectance value can be caused by the surface roughness.

The sensor response to the small ammonia concentrations in water is plotted in Fig. 7. As one can see, the changes in the complex dielectric function of the sensitive layer caused by the ammonia inclusions due to the analyte adsorption within $SnO_2$ film, resulting in an increase of the fiber-film reflectance and, in turn, the sensor normalized signal. Strong increase of sensor signal was observed at small concentrations and saturation has been reached under about 20 ppm of ammonia. Quick saturation can be caused by small surface area (the diameter of fiber core is about 9 μm). Response times of approximately 15 min were observed. We suppose that reduction of the film thickness and increase of the film porosity can induce a significant reduction of the response time and increase the range of detectable concentrations.

The sensor output exhibits the typical behaviour of the analyte diffusion within the sensing coating. Detailed information on the sensor sensitivity can be obtained from Fig. 8 where the calibration curve is shown in terms of relative reflectance changes. It is worth to note that a non-linear dependence of the optoelectronic normalized signal on the ammonia concentration demonstrated the increase of approximately 3 % for an overall ammonia concentration of 20 ppm. Considering the minimum detectable normalized signal, the detection limit close to a sub-ppm level has been obtained.

## 4. Conclusion

In summary, a novel $SnO_2$ based optical sensor for in-water ammonia detection at room temperature has been demonstrated. The combination of the excellent sensing properties of MO films with the potentiality of the optical fiber technology was proposed to develop a novel class of sensors able to operate in water and at room temperature. Tin-dioxide films were successfully deposited onto the distant end of single-mode SOF by the electrostatic spray pyrolysis deposition technique. The fabricated sensors were employed in a reflectometric system involving single wavelength reflectance measurements for testing the sensing performances. Here, the experimental results are reported on the sensor capability to detect the ppm ammonia concentrations in water at room temperature. Fast time response in the minute range and sub-ppm resolution were demonstrated. The appropriate functionalization of the sensing coatings and the reduction of the film thickness would allow tailoring the sensor features in terms of response time, sensitivity and chemical specificity to be used in water and environmental monitoring.

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