1st International Conference on Sensing Technology
November 21-23, 2005 Palmerston North, New Zealand

Sensing Properties of Ultra-Thin Films of Single Walled Carbon Nanotubes Investigated by Optical Fiber and Acoustic Devices: Towards New VOCs Sensors

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Abstract

We present a study of the sensitivity to Volatile Organic Compounds (VOCs), such as toluene, xylene and tetrahydrofuran (THF), of standard Silica Optical Fiber (SOF) and Quartz Crystal Microbalance (QCM) sensors incorporating Langmuir-Blodgett (LB) ultra-thin films of Single-Walled Carbon Nanotubes (SWCNTs). A clear dependency of the optical and acoustic sensors sensitivities on the nanomaterial thickness is demonstrated. The sensors based on SWCNTs provide high sensitivity, very low limits of VOCs detection, fast response and good repeatability, at room temperature.

Keywords: Carbon nanotubes, optical fiber VOCs sensors, QCM acoustic VOCs sensors

1 Introduction

The single-walled carbon nanotubes (SWCNTs) are advanced nanostructured materials with promising sensing properties in terms of sensitivity, low sub-ppm limit of detection, on-line and real-time vapor detection, at room temperature [1,2]. They possess unique electronic, optical, mechanical and thermal characteristics. The ability of this material to exist in a very fine powdered form with highly porous structure, their nanosized morphology (diameter 1-10 nm) and high surface area (100-1800 m2/g), and the existence of particular chemical interactions between carbon atoms and gas molecules, make them strongly attractive and very promising as gas sensor nanomaterials.

The SWCNTs have already been used as sensitive nanomaterials for the detection of VOCs by using standard SOFs based on light reflectometry at a wavelength of 1310 nm and QCM 10 MHz AT-cut quartz resonators. The transducing principles were based respectively on complex dielectric function and mass change induced by target analyte molecules adsorption [2,3].

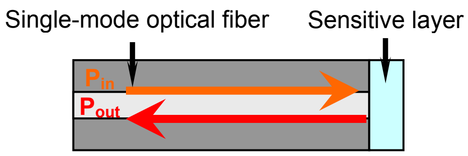
Differently from previous works, where cadmium arachidate (CdA) buffer layers were used, here, multilayers of SWCNTs with different thickness were successfully transferred directly onto the sensors surfaces. A study of the sensitivities of the optical and acoustic sensors to toluene, xylene and tetrahydrofuran is presented, demonstrating the possibility to appropriately tailor the sensor responses by changing the nanomaterial thickness.

The behavior of the SOF sensor response when the relative humidity content inside the test chamber changes from 38% to 14%, at constant temperature (~28°C), is also presented. The dependence was found to be almost linear and allows to compensate eventual relative humidity changes during the testing of vapors exposure.

Furthermore a significant improvement in the identification of organic vapors can be achieved by combining the responses of the various modules of QCM and SOF sensors. In fact, the data fusion from the optical and acoustic chemical sensors, coated by the same sensitive nanomaterial, based on complementary transducing principles can significantly improve the recognition and discrimination capability of the multi-transducer hybrid system by means of pattern recognition techniques [4].

2 Principles And Methods

The key point of the SOF sensors is the dependence of the reflectance on the film features such as the complex dielectric function and the thickness. Thus, changes in these parameters due to the molecules adsorption into the film leads to variations in the reflected power at the film interface (Fig. 1). In order to provide accurate measurements, not dependent on the optical power levels along the measure chain, a normalized sensor output was considered. In particular, the reflected power was normalized to the power emitted by the source [3]. The introduction of a multi-channel fiber optic switch allows the simultaneous monitoring of up to 8 SOF sensors.

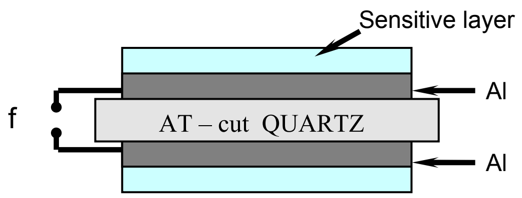


$$\Delta R_{film} = f\,(\Delta\varepsilon_{Film}\,,\,\Delta d_{Film}) \qquad \text{Eq. 1}$$

- R_{film} is the fiber-film interface reflectance
- ε_{Film} is the complex dielectric constant of the film
- d_{Film} is the film thickness

Figure 1: Schematic view of the optical fiber sensor.

With regards to acoustic sensors, the principle of a QCM sensor is that a mass added or removed from a vibrating body changes its resonant frequency. Upon vapors exposure, the analyte molecules are adsorbed by the sensitive overlayer deposited onto the QCM device, causing its mass loading and, in turn, changes in the fundamental oscillation frequency, taken as the sensors output (Fig. 2).



$$\Delta f = -C_q f_0^2 \Delta m = -\frac{2 f_0^2 \Delta m}{A\sqrt{\mu_q \rho_q}} \qquad Eq.\ 2$$

- C_q is the mass sensitivity constant of the substrate
- μ_q is the substrate shear modulus
- ρ_q is the substrate density

Figure 2: Schematic view of the acoustic QCM sensor.

The output frequencies have been measured by a frequency counter with a multiplexed read-out by a switch unit driving two 50Ω 4x1 rf multiplexers.

The molecular engineering LB technique has been used for depositing SWCNTs films, with thickness in the range 4-40 nm, onto a CdA buffer layer and directly onto the bare substrates of the optical SOF and acoustic QCM sensors. More details about the deposition parameters can be found elsewhere [2,3].

3 Experimental Results

In Fig. 3, the time responses of the SOF and QCM sensors coated by 4 monolayers of SWCNTs (~8 nm) exposed, at room temperature, to decreasing

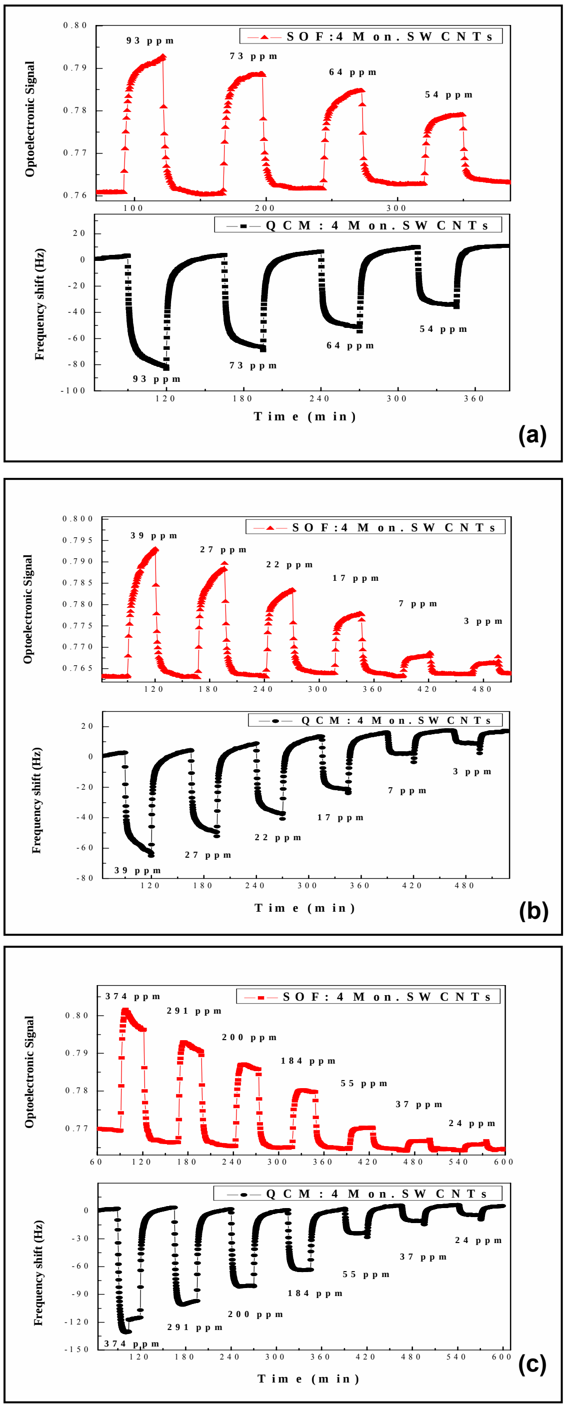
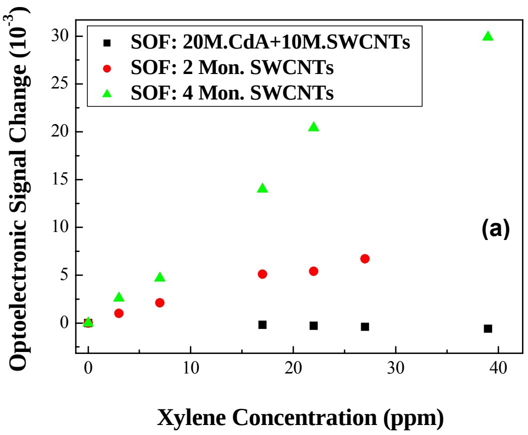


Figure 3: Transient responses of the SOF (upper curves) and QCM (lower curves) sensors, coated by 4 monolayers of SWCNTs, to (a) toluene, (b) xylene and (c) THF vapors with concentrations in the range 3-380 ppm, at room temperature.

concentrations of (a) toluene, (b) xylene and (c) THF vapors are reported. The results obtained indicate that acoustic and optical sensors incorporating SWCNTs provide high sensitivity and fast responses, taking into account the volume of the test chamber (~1200 ml). They also demonstrate that after each dynamic adsorption-desorption cycle (dry air – VOCs vapors – dry air) the baseline output signals are totally recovered and highly stable.

The calibration curves for three SOF and QCM sensors, two of which coated only by SWCNTs films and one coated by a multilayer of CdA buffer material and SWCNTs, exposed to 30 minutes pulses of xylene, have been reported in Fig. 4.



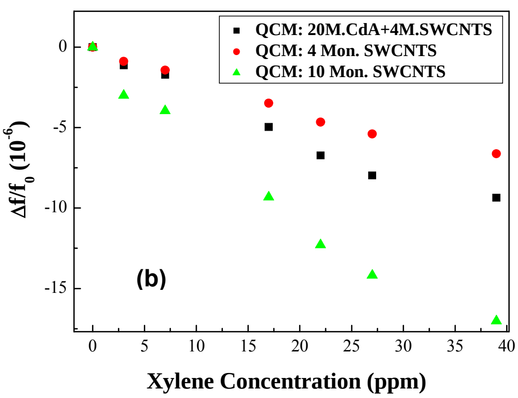


Figure 4: Calibration curves for (a) 3 SOF and (b) 3 QCM sensors exposed, at room temperature, to xylene vapors with concentrations in the range 3-39 ppm: the 3 SOF sensors were coated by 10 monolayers of SWCNTs onto 20 monolayers of CdA, 2 and 4 monolayers of SWCNTs; while the 3 QCM sensors were coated by 4 monolayers of SWCNTs onto 20 monolayers of CdA, 4 and 10 monolayers of SWCNTs.

Here, for each acoustic sensor the normalized frequency shifts $\Delta f/f_0$ (expressed as a frequency shift normalized to the steady state oscillation frequency) versus the xylene vapor concentrations have been plotted. As can be seen, a clear dependency of the optical and acoustic sensors sensitivities on the nanomaterial thickness has been found. In fact, the higher is the thickness of SWCNTs films deposited onto the SOF and QCM sensors, the higher is the sensors response to targeted analyte tested.

This effect has also been observed for the other VOCs examined and it means that the sensitivity to a target analyte can be tailored by appropriately choosing the overlayer thickness.

Differently from the QCM sensors, where the buffer CdA material increases the sensors response for the same thickness of SWCNTs overlayer (see Fig. 4b); in the case of the SOF transducers, it strongly reduces the sensors sensitivity (see Fig. 4a). In addition, the optical properties of the buffer layer could not be optimized to improve the optical sensor sensitivity. Furthermore, while for the optical sensors coated by 2 and 4 monolayers of SWCNTs the response increases upon exposure, the SOF probe coated by SWCNTs onto the CdA buffer layer shows a reversed response to all the tested VOCs. It can be attributed to the different model for the reflectance that has to be taken into account in the two cases: a 3-layer model (optical fiber - SWCNTs film - external medium) in the first case, and a 4-layer model (optical fiber - CdA buffer - SWCNTs film - external medium) in the second one [5].

A repeatability test has been carried out by exposing the SOF and QCM sensors coated by 4 monolayers of SWCNTs three times to the same pulse of 20 ppm of xylene vapors. The results obtained are reported in Fig. 5 and demonstrate that a very good repeatability has been achieved for both optical and acoustic sensors

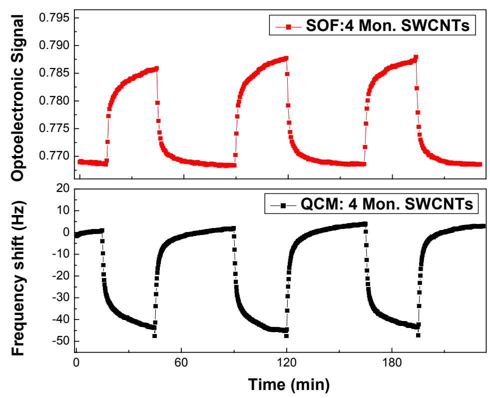


Figure 5: Repeatability of SOF (upper curve) and QCM (lower curve) sensors, coated by 4 monolayers of SWCNTs, and consecutively three-time exposed to the same concentration of 20 ppm xylene, at room temperature.

Fig. 6 reports the output signal of the SOF sensor coated by 2 monolayers of SWCNTs onto 20 monolayers of CdA when the relative humidity inside the test chamber decreases from 38% to 14%, at constant temperature (27.9-28.2°C). As can be seen, the sensor incorporating SWCNTs is also a water molecules adsorbent, and shows a quite linear relationship between the sensor signal and the relative humidity content, as highlighted in Fig. 7.

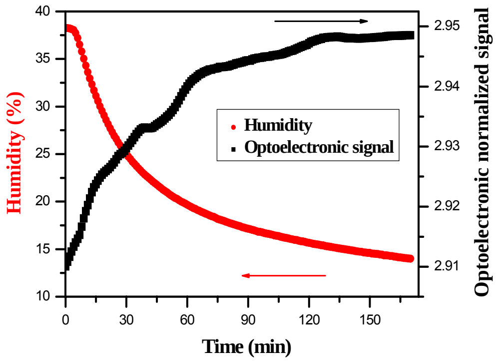


Figure 6: Time behaviour of the output signal of the SOF sensor coated by 2 monolayers of SWCNTs onto 20 monolayers of CdA to decreasing relative humidity content, at constant temperature.

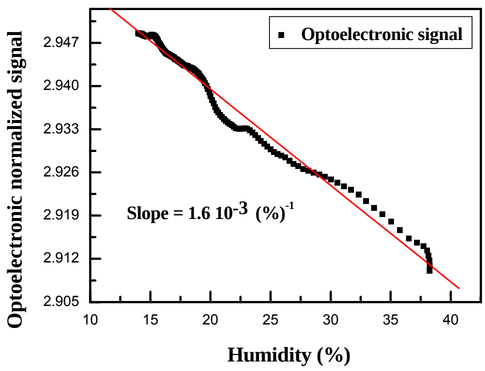


Figure 7: Calibration curve of the SOF sensor coated by 2 monolayers of SWCNTs onto 20 monolayers of CdA to the relative humidity, at room temperature.

These results can be used to compensate unwanted optoelectronic signal changes due to the influence of the relative humidity in the test ambient upon exposure to a given analyte.

Finally, the data fusion between chemical sensors, coated by the same sensitive nanomaterial, with different transducing principles could be very useful in order to enhance the features extraction from multi-component mixtures in vapor recognition and discrimination applications using pattern recognition techniques such as Principal Component Analysis (PCA) and Artificial Neural Networks (ANNs) [6].

4 Conclusions

In summary, SOF optical and QCM acoustic sensors incorporating films of single-walled carbon nanotubes as highly sensitive coatings for VOCs detection, have been simultaneously tested to toluene, xylene and tetrahydrofuran individual vapors in order to study the dependence of the optical and acoustic sensors sensitivities on the nanomaterial thickness. To this aim, SWCNTs thin films with different thickness have been deposited directly onto both SOF and QCM sensors and onto a buffer-linker multilayer of CdA, using the molecular engineering Langmuir-Blodgett advanced deposition technique. The tests, carried out at room temperature by exposing the sensing probes to dynamic adsorption-desorption cycles, demonstrate that the SOF optical and QCM acoustic sensors based on SWCNTs provide high sensitivity, very low limits of VOCs detection, repeatability, good stability, fast response, and show a clear dependency of the sensors sensitivities on the nanomaterial thickness. Differently from acoustic sensors, opposite behavior of the optoelectronic output signal can be obtained by using SOF sensors with or without the CdA buffer-linker material, giving the possibility to tailor the sensors sensitivity for the specific vapor sensing applications.

The behaviour of the SOF sensors output to relative humidity changes in the test ambient, at constant temperature, has also been reported, showing a linear dependency of the optoelectronic signal on the relative humidity content, making it possible to compensate eventual optical signal changes due not to the target molecules adsorption, but to relative humidity changes during the exposure to vapors.

In addition, the correlation between the acoustic and optical data can be useful in order to characterize the optical changes due to the adsorption of the given VOCs. Finally, proper data fusion is actually under investigation to enhance the features extraction when more analytes are adsorbed.

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