

NO₂ QCM gas sensor based on electrochemical deposition of PEDOT

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ABSTRACT

In this paper the authors describe the development and the characterization of a Quartz Crystal Microbalance (QCM) sensor for NO₂ detection with the sensitive layer made of a thin films of poly (3,4-ethylenedioxythiophene) (PEDOT). The PEDOT layer was obtained by electropolymerization on one of the gold electrodes of a 10 MHz AT-cut commercial quartz crystal. The sensor performance in terms of sensitivity and selectivity were assessed exploiting an ad hoc chemical sampling unit, and a low noise conditioning and processing electronic system. This latter consists of an oscillator hosting the piezoelectric resonator, and of a frequency measurement system granting a (short time) relative accuracy of approximately 10⁻⁸, which ensures a mass resolution in the order of the ng. The preliminary obtained results show a NO₂ resolution and sensitivity of the order of 1 ppm, and 2.6 Hz/ppm, respectively, at 35 °C constant room temperature and in a dry environment, and show that a satisfactory repeatability can be achieved with recovery cycles in N₂ at room temperature.

INTRODUCTION

Nitrogen Oxides derivatives (NO_x) are commonly generated by combustion processes. Dioxide nitrogen (NO₂) is a highly toxic gas, and one of the main causes of air pollution. Low concentrations of NO₂ (a few ppm) are harmful for human beings and plants. For this reason there is a large request for sensitive NO₂ detection systems suitable for continuous air-quality monitoring. The scientific community is studying new solutions to detect NO_x, based on different kinds of chemical sensors.

Among the different chemical sensor families available for this purpose, piezoelectric sensors are good candidates due to the high mass sensitivity they exhibit. Several sensors of this type, including surface acoustic wave (SAW) devices, have been developed in the last years for the specific detection of various chemical and biological molecules in liquid or gaseous media. All these sensors are based on a piezoelectric acoustic resonator covered by a sensing layer that selectively adsorbs materials from the atmosphere, therefore changing the physical parameters of the resonator and affecting the resonance frequency, and/or the acoustic wave properties. In particular, the binding of a substance to the resonating structure causes a down-shift of the resonant frequency of

the device. QCM sensors exploit this effect: a shift in the resonant frequency of a quartz oscillator, usually a thin disc-shape quartz crystal, can be attributed to the mass bound to the sensor surface. The oscillation frequency shift, for an AT-cut crystal with two metal electrodes deposited on two opposite sides of the crystal can be simply expressed, under some assumptions summarized hereafter, by the Sauerbrey equation:

$$\Delta f = -\frac{2f_0^2 \Delta m}{A\sqrt{\rho_q \mu_q}} \quad (1)$$

where f_0 is the fundamental resonant frequency, A the piezoelectrically active area defined by the two electrodes, ρ_q the density (2.648 10³ kg/m³) and μ_q the shear modulus (2.947 10¹⁰ N/m²) of quartz.

The Sauerbrey equation is found by treating the film and the adsorbed mass as an extension of the quartz, and it only applies to systems in which (a) the deposited mass has the same acoustic properties as the crystal and (b) the frequency shift is small with respect to f_0 ($\Delta f_0 / f_0 < 5\%$). In any case, as long as these assumptions hold, the simple relationship between the change in frequency (Δf) and the change in mass (Δm) encourage using QCM in many chemical sensing applications.

Modification of QCM surfaces with various polymeric sensing materials is reported in literature. Nevertheless, up to now a few QCM-type (including SAW devices) NO₂ gas sensors have been developed due to the poor sensitivity and/or gas selectivity of the studied sensing materials (see reference [1] and the references herein), that are additional limits to the high sensitivity to environmental conditions (humidity, temperature, mechanical stresses) presented in general by these kind of sensors. On the other hand, polymer films have been widely studied for the development of conductivity variation sensors, and several works were devoted to NO₂ detection. In comparison with most of commercially available sensors, based on metal oxide, the sensors made of conducting polymers have high sensitivity, short response time and can work at room temperature. Different works can be found in literature describing several polymer deposition techniques and discussing the NO₂ sensing properties of different polymers. As an example Ram et al. [2] have focused their attention on the use of organized ultrathin films of conducting polymers which selectively recognize NO₂; in particular they focus their attention on Polyhexylthiophene(PHTh), poly(ethylenedioxythiophene) (PEDOT), PHTh-PEDOT copolymer, sulfonated polyaniline, polyaniline (PANI)-

SnO₂, polypyrrole(PPy)-SnO₂, PEDOT-SnO₂, PHTH-SnO₂ and copolymer (HTh-EDT)-SnO₂ conducting polymers. In [2] gas detection via resistance variation measurements was taken into account, a mechanism of interaction between polymer and molecules of gas was proposed. Others authors (see e.g. Dan Li et al. [3]) proposed electro active nanocomposite ultrathin films of polyanilin (PAN) and isopolymolybdic acid (PMA) fabricated by a novel molecular self-assembling process based on the alternate deposition of PAN and PMA from their dilute solutions. It was found that the conductivity of the PAN films is sensitive to humidity, NO₂ and NH₃. Yan X.B. et al. [4] proposed a chemical sensor for NO₂ detection using polyaniline nanofibres. In the last decade, thiophene-based conducting polymers have been extensively studied, especially PEDOT for its excellent environmental stability, its low oxidation potential and low band gap. Zeng et al. [5] proposed a NO₂ gas sensors constructed by depositing PEDOT films on the surface of interdigitated electrodes. The tests reported in [5] indicated that the resistance of the films increased with the increase of NO₂ concentration. Henkel et al. [6] proposed a quartz microbalance produced with PEDOT and polypyrrole as an electrode, and tested it with NO₂ in the range 10-100 ppm.

Even if, as discussed before, QCM polymer based NO₂ sensors did not have yet a large diffusion, the relevant amount of results reported in the literature concerning NO₂ sensing with polymer layers encourage further work about this subject. On this basis, in this paper the authors describe the development and the encouraging preliminary tests of a Quartz Crystal Microbalance (QCM) sensor for NO₂ detection with the sensitive layer made of a thin film of PEDOT. The PEDOT was obtained by electropolymerization on one of the gold electrodes of a 10 MHz AT-cut commercial quartz crystal. The adopted electropolymerization technique allowed obtaining highly controlled and highly reproducible morphological characteristics of the sensing layer, as it was proved by Atomic Force Microscopy (AFM) studies [7-9]. These studies allowed for controlling the polymer deposition process (by changing the polymerisation variables such as substrates, solvents, supporting electrolytes, temperature, etc.) in order to obtain thin films with the desired characteristics.

The sensor performance in terms of sensitivity and selectivity was assessed exploiting an ad hoc chemical sampling unit, and a low noise conditioning and processing electronic system. This latter consists of an oscillator hosting the piezoelectric resonator, and of a frequency measurement system granting a (short time) relative accuracy of approximately 10⁻⁸, which ensures a mass resolution in the order of the ng. The preliminary obtained results show a NO₂ resolution and sensitivity of the order of 1 ppm, and 2.6 Hz/ppm, respectively, at 35 °C constant room temperature and 0% relative humidity, and show that a satisfactory repeatability can be achieved with recovery cycles in N₂ at room temperature.

The paper is organized as follows: in section I the realization of the PEDOT sensing layer is described; in

section II the measurement setup, including the chemical sampling and the low noise conditioning and processing electronic systems are described; in section III the obtained preliminary results are presented and discussed. Conclusions and references close the paper.

PREPARATION OF THE PEDOT QCM SENSORS

The reagents used to prepare the sensing layer were EDOT (Aldrich) and TEAPF₆ (Fluka, puriss.). Anhydrous acetonitrile (Aldrich, 99.8% pure, packaged under nitrogen) was used as solvent. AT-cut commercial 10 MHz quartz crystals (L.O.T. Orieli Italia s.r.l.) with vapour-deposited 0.39-cm² gold electrodes, housed in HC48 packages, were used as basic elements for the QCM sensors.

The electropolymerization process used for the deposition of the sensing layer on one of the quartz gold electrodes allows to control and standardize the deposition process, and to obtain sensing layers with a high reproducibility degree. Electropolymerization was performed at room temperature in a N₂ atmosphere, using a single-compartment, three-electrode cell. A glassy carbon rod was used as counter electrode and an Ag/AgCl electrode as reference electrode. The working electrode was one of the gold electrodes of the above mentioned 10 MHz AT-cut quartz crystal. The electropolymerization processes were performed in 10 mmol/L EDOT, 0.1 mol/L TEAPF₆, CH₃CN solution. In the potentiodynamic growth, the polymer-modified electrodes were prepared by repeatedly cycling the potential between -0.5 V and +1.25 V, i.e. the value at which oxidation of the starting monomer occurs. A potential scan rate of 0.05 V/s was used in all the experiments.

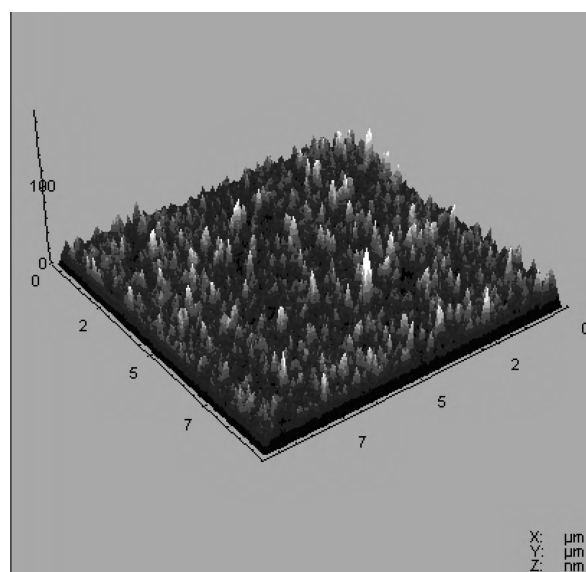


Figure 1. 3D not filtered AFM image of PEDOT potentiodynamically grown in 0.1 mol/L TEAPF₆, CH₃CN solution.

The sensing layer topography was measured *ex situ*, using a Molecular Imaging AFM instrument (PicoSPM, Molecular Imaging) operating in contact mode, with a commercial Si₃N₄ cantilever (Nanosensors, Wetzlar-Blankenfeld). The surfaces of bare Au and of polymeric deposits were characterised by non-filtered 512×512 pixel images with area 10 μm ×10 μm .

MEASUREMENT SET UP

The QCM sensors were tested using an ad hoc developed measurement system that is composed of a chemical sampling and control system, of a dedicated front end electronics, and of a PC (fig. 2). During measurements the chemical sampling and control system allows to maintain the sensors in known and predefined conditions in terms of chemical atmosphere and temperature. Humidity is monitored by a dedicated acquisition channel. The chemical sampling system is based on a set of gas tanks feeding a bench of PC controlled flow-meters (BronkHorst F-201C). The combination of the controlled flows (carrier gas and mixtures under test) is sent to the measurement chamber that is placed in an oven kept at a reference temperature (1°C accuracy). The measurement chamber is made of Teflon, it is realized in a circular symmetry, and it allows performing measurements with two sensors and two reference quartzes, it contains a humidity sensor and a temperature sensor (J thermocouple).

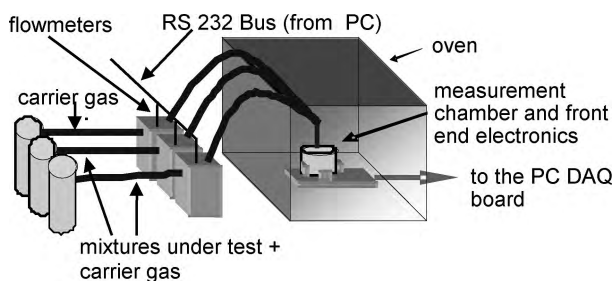


Figure 2. Block scheme of the QCM measurement system

The chamber is directly connected to the front end electronics (fig. 3), that consists of two oscillators for low Q quartzes, two oscillators for reference quartzes and two mixers. The system is designed to perform measurements with quartz with resonance frequency in the range 5MHz - 15 MHz. It allows measuring the frequency difference between the output signal of the sensor based oscillator, and the output signal of the reference quartz based oscillator. The frequency shift measurement system is based on a commercial DAQ board that acquires the mixer output signal, and on a single tone frequency digital estimation algorithm. The accuracy of the frequency shift measurement is 0.1 Hz in a range of 40 kHz. A dedicated virtual instrument on the PC allows to simultaneously control the chemical sampling system, and to process and display the measurement results. With this system it is

possible to perform measurements in chemical steady conditions or during chemical transients.

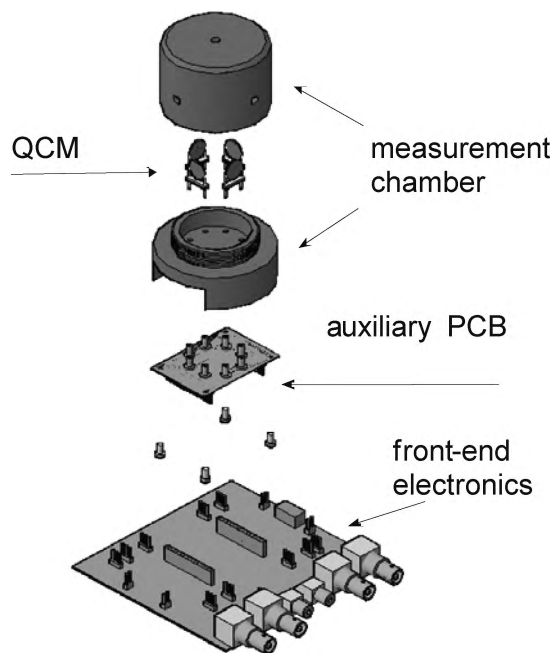


Figure 3. QCM measurement chamber and front end electronics PCB

PRELIMINARY EXPERIMENTAL RESULTS

A set of 6 nominally equal sensors obtained as described in section II was tested for NO₂ sensitivity (in the range 2 ppm - 10 ppm). Tests were also conducted to investigate the sensitivity to CO and O₂, and to evaluate the effects of environmental conditions, such as gas flow variations.

The frequency shift of each QCM sensor with respect to a reference quartz in the same environmental conditions was measured during chemical transients obtained with the following measurement protocol. Phase 0: exposure to reference gas (N₂, duration 120s); phase 1: exposure to the gas under test (180s), and phase 2: recovery in N₂ (600s). In these three phases a constant gas flow of 200mL/min was used, at a 35 °C constant room temperature and 0% relative humidity. In general N repetitions of phase 1 and phase 2 were scheduled during measurements, changing the concentration of the gas under test in phase 1 by suitably mixing two gas flows (N₂ and gas under test mixture + N₂). An example of the responses obtained with one of the tested sensors to a chemical pulse of 2.3 ppm of NO₂ is shown in fig 4 (analogous results were obtained with all the six sensors). During repeated measurements with the selected protocol and NO₂ concentrations in the range 1-10 ppm the sensor showed a slow drift of the baseline indicating a not complete desorption of NO₂, hence long cleaning cycles were used to recover the initial conditions after 4-5 repetitions of the measurement cycles (depending on the used NO₂

concentrations). The test results are encouraging, as it can be deduced from fig. 5, where the obtained frequency shifts are plotted versus the NO₂ concentration for the same sensor of fig. 4. It can be seen in fig. 5 that the sensor shows a NO₂ sensitivity of the order of 2.6 Hz/ppm, as well as a satisfactory linearity, whereas the resolution is in the order of 1 ppm, due also to the high (short time) relative accuracy of the frequency measurement that is approximately 10⁻⁸. Preliminary tests for the sensitivity to interfering gasses such as CO and O₂ were also performed, showing a good sensor selectivity toward NO₂. The sensors show a maximum frequency shift of 10 Hz when chemical pulses of 300 ppm of CO and 10000 ppm of O₂ are applied, that is a sensitivity to CO and O₂ at least one order and three order of magnitude lower than the sensitivity to NO₂, respectively.

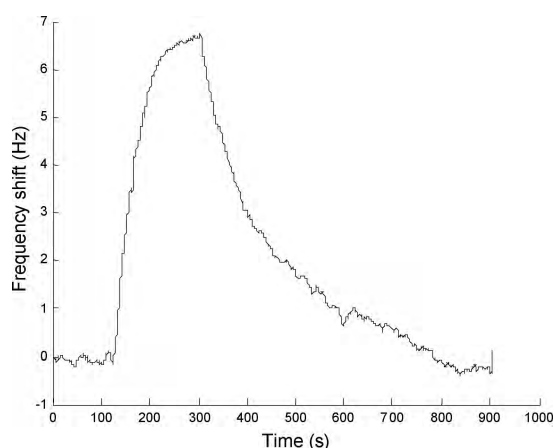


Fig.4. QCM sensor response to 2.3 ppm NO₂ in N₂ applied between $t_1=120$ s and $t_2=300$ s (room temperature 35 °C, 0% RH, total flow 200 mL/min).

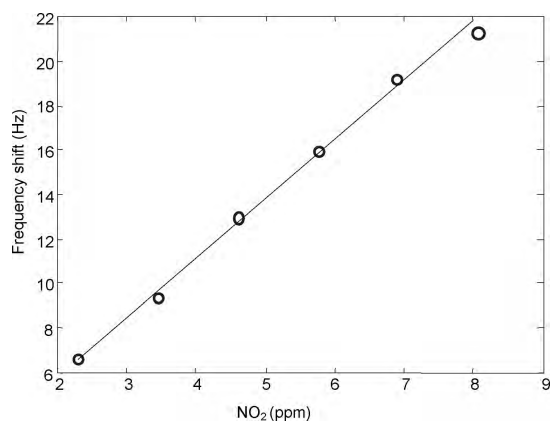


Fig.5. QCM sensor response in the range 2 ppm -10 ppm NO₂ in N₂. Measurement condition: room temperature 35 °C, 0% RH, total flow 200 mL/min.

CONCLUSIONS

In this paper the authors describe the development and the preliminary tests of a Quartz Crystal Microbalance (QCM) sensor for NO₂ detection with the

sensitive layer made of a thin films of PEDOT. A sensitivity to NO₂ of the order of 2.6 Hz/ppm (at 35 °C constant room temperature and 0% relative humidity) was verified with an ad hoc developed measurement instrument, that grants a NO₂ resolution in the order of 1 ppm. The preliminary tests show also a good selectivity of the sensor to NO₂. A further issue currently studied is how to reduce the duration of the recovery cycles at present required to obtain repeatable measurements.

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