QCM Sensors Based on In_2O_3 Nano-films Obtained by a Pulsed Plasma Deposition Technique

Tommaso Addabbo, Andrea Baldi, Mara Bruzzi, Ada Fort, Marco Mugnaini and Valerio Vignoli

Abstract In this paper Quartz Crystal Microbalance (QCM) gas sensors obtained depositing nano-films of In_2O_3 over AT-cut 10 MHz resonators are presented. Films are grown by a Low-Temperature Pulsed Electron Deposition (LTPED), a single-stage growth technology by which films can be deposited on a variety of different substrates Rampino et al. (Appl Phys Lett 101(13):132107, 2012 [1]) down to a few nms thickness, allowing for maintaining large quality factors of the quartzes and for realizing very stable oscillators. The gas sensing performance of these devices are studied by means of experiments with a toxic gas, NO_2, water vapor and ethanol. The effect of UV irradiation on the sensor response is also studied. The sensors provide stable and repeatable measurements, a large response to water vapor, and respond reversibly to NO_2.

Keywords Quartz crystal microbalance · Gas sensors · Nano-film · In_2O_3

1 Introduction

In the last years the research has shown that In_2O_3 is a promising material for gas-sensor applications. In particular gas sensors based on In_2O_3 are suitable for the detection of low concentrations of oxidizing gases like O_3, NO_x and Cl_2 [2]. On the other hand, it was shown that in some cases In_2O_3-based gas sensors may have sufficient sensitivity and good selectivity also toward some reducing gases (such as CO in the presence of H_2) depending on the preparation route and on the surface stoichiometry. It must be underlined that in general for metal oxide gas sensors the

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preparation route and/or the deposition method are largely influent on the sensor performance, because sensing is strongly dependent on both defect chemistry and micro/nanostructure.

For the deposition of In_2O_3 nano-structured films many different techniques have been proposed such as: chemical vapor deposition; thermal oxidation of In films; spray pyrolysis; sol–gel; atomic layer deposition; pulsed laser ablation; DC and RF-sputtering. These techniques generally require a complex processing for precursors to be formed in the environment of the deposition chamber. In this work we used a novel deposition method, the Low Temperature Pulsed Electron Deposition (LTPED) technique. A pulsed high density electron beam (500 MW/cm^2), interacting with the target, causes material ablation independently of the energy gap (i.e. the optical absorption) of the target itself. The chemical composition of the target is then transferred by a supersonic highly energetic plasma giving rise to thin films directly on the substrate while keeping a low substrate temperature. This technique [1] can grow films both on metal and dielectric substrates, down to a controlled few-nms thickness, with a low-cost process and essentially no need for post-deposition treatments, like high-temperature annealing of the substrate [1].

In this work we describe, characterize and study nano-layers of In_2O_3, used as sensitive layers in a quartz crystal microbalance (QCM). QCMs (unless adopting special piezoelectric resonators) operate at room temperature. For this reason, since usually In_2O_3 is used in resistive chemical sensors, that operate at high temperatures and base their operations on chemisorption, the feasibility of a In_2O_3 QCM gas sensor has to be investigated. Note that even if at RT chemisorption on metal oxides is very limited, physisorption is favored, therefore an adsorption on the sensitive film is possible.

As far as the sensitivity is concerned it must be noted that, in case of adsorption of a gas monolayer, a rough approximation of the maximum adsorbed mass, obtained considering the adsorption on a plane surface and a full coverage of the surface, is of some ng for light molecules. Therefore, the maximum expected frequency shift due to gas adsorption is in the order of some Hertzs. This seems to set a limit to the use of this device for gas sensing applications, but by depositing a very thin sensitive layer by means of LTPED, we can maintain a very large value of the Q of the quartz, which allows to reach very high frequency resolutions. In fact, frequency stability and noise of a quartz oscillator are related to the Q-factor: the larger is the Q factor the more immune to parasitic effects is the oscillator and the smaller is the resultant frequency noise.

2 Measurement System Description

A thin layer of In_2O_3 with a thickness of about 40 nm has been deposited on an AT-cut 10 MHz quartz disk with a diameter of 6 mm and two Au electrodes.

The response of the gas sensor is due to the adsorption of gas on the In_2O_3 layer increasing the mass of the electromechanical resonator. Sauerbrey equation relates the resonance frequency shift Δf to the mass adsorbed Δm as follows [3, 4]:

$$\Delta f = \frac{-2f_0^2}{A\sqrt{\mu_q \rho_q}} \Delta m \Rightarrow |\Delta f|[\text{Hz}] = 800\,\Delta m[\mu\text{g}] \tag{1}$$

which can be also written as:

$$\Delta m[n\text{g}] = 1.25|\Delta f|[\text{Hz}] \tag{2}$$

where f_0 is the quartz resonance frequency in Hz (10 MHz), A is the effective area of the electrodes (28×10^{-6} m^2), ρ_q is the quartz density (2.648 g cm^{-3}), μ_q is the shear module for AT-cut quartzes (2.947×10^{11} g cm^{-1} s^{-2}).

As far as the sensitivity is concerned it must be noted that, in case of adsorption of a gas monolayer, a rough approximation of the maximum adsorbed mass, obtained considering the adsorption on a plane surface with the area of the electrode and a full coverage of the surface (adsorbed molecules density in the order of magnitude of 10^{14} cm^{-2}) is about 7 ng for H_2O, 19 ng for CO and 11 ng for NO_2. Therefore the maximum expected frequency shift is in the order of some Hertzs. The characterization system shown in Fig. 1 [5] was used to test the developed sensor. It consists of an accurate frequency meter and a gas delivering system. The quartz oscillator is inserted in a high resolution measurement system of the frequency shift, which grants a resolution lower than 0.1 Hz.

The gas system used to test the sensor is able to deliver a gas mixture with an accurately controlled composition in a Teflon measurement chamber. Three PC-controlled flow-meters establish the flow from certified gas cylinders containing the components of the gas mixture. The total flow during a measurement is constant

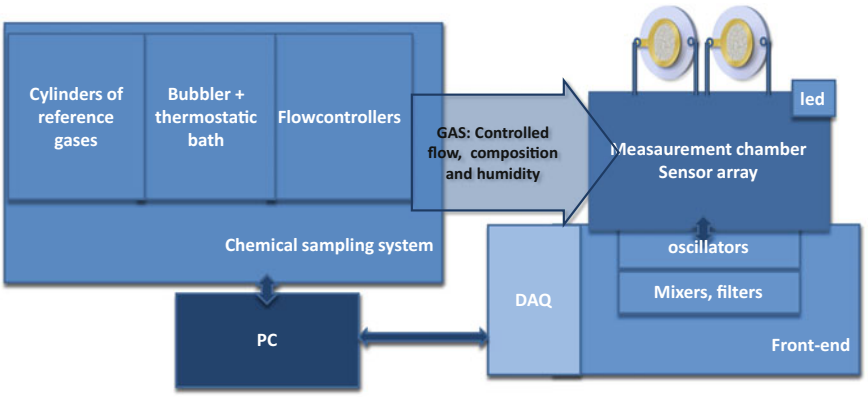

Fig. 1 Measurement system

(100 mL/min in this work) whereas its composition can dynamically change during a measurement.

Either humidity or ethanol partial pressure are set by means of a bubbler containing ultrapure water (ethanol), kept at a known temperature, in which a dry carrier gas is saturated; the desired partial pressure of water (ethanol) is obtained by mixing the flow from the bubbler with the dry carrier gas flow.

The measurement system allows for testing the sensor under UV radiation, for this purpose a led with a peak wavelength of 275 nm was placed in the measurement chamber.

3 Experimental Results and Discussion

Some experimental results are reported in Fig. 2. In the top plot the response of the sensor defined as the frequency shift reached at the end of a fixed time (8 min) of exposure to the target gas is shown. Responses to different test gases are plotted as a function of time in the bottom plot. These latter are obtained by changing the concentration of a test gas in a carrier gas (N_2) according to the protocol described in the figure caption. The response to water vapor is obtained with four pulses of humid N_2 with the following values of relative humidity: 100, 50, 30%. Sensors response to water vapor can be explained by multi-layer adsorption, whereas NO_2 response can be explained by a single layer reversible adsorption. Note that NO_2 adsorption is highly influenced by the presence of humidity, which enhances the sensitivity toward the target gas. As can be seen in Fig. 2, in presence of water the response to NO_2 assumes a complex shape indicating an interaction between the

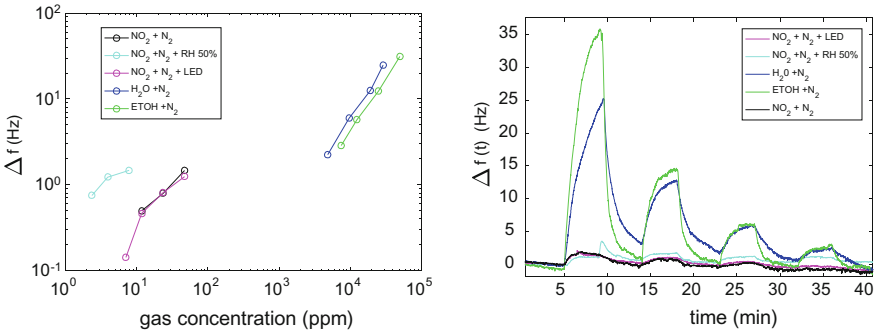

Fig. 2 QCM responses to different test gases. *Left* responses as a function of target gas concentration. *Right* transient responses to different target gas pulses (4 min carrier gas, 8 min target gas + carrier gas concentration #1, 4 min carrier gas, 8 min target gas + carrier gas concentration #2, 4 min carrier gas, 8 min target gas + carrier gas concentration #3, 4 min carrier gas, 8 min target gas + carrier gas concentration #4, 4 min carrier gas, total flow 100 mL/min. The concentration delivered to the test chamber for the different gases are those shown in the leftmost plots

two species and the sensor behavior can no more be explained by simple adsorption-desorption reactions. On the other hand, UV radiation with this power and wavelength doesn't affect the response to NO_2. The sensor was tested also with CO, giving an almost negligible frequency shifts.

4 Conclusions

In this work we present first studies on gas sensing properties of In_2O_3 nano-layers on quartz crystal microbalances (QCMs). A 40 nm-film deposited by LTPED on QCM was tested at room temperature under controlled flows of different gas kinds and concentrations. Experimental results showed that the devices are sensitive to NO_2 and water vapour, while negligible effects are observed in presence of CO. The response to NO_2 is highly dependent on the relative humidity. Moreover, the experimental results show that the response can't in general be explained by simple adsorption-desorption reactions. The developed device can be used as humidity sensor, whereas the application to NO_2 detection needs a controlled humidity environment.

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