Influence of loading QCMs with electrochemically-deposited ZnO on their NO\textsubscript{2}-sensing properties

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Abstract. This paper reports on ZnO layers’ sensitivity to NO\textsubscript{2} exposure. ZnO layers were grown by electrochemical deposition on the surface of quartz crystal microbalances (QCMs) with Au electrodes; the sensitivity was estimated by the frequency-time characteristics (FTCs) of the QCM, namely, its resonance-frequency-shift response. The sorption process was investigated in NO\textsubscript{2} test gas. The behavior was studied of three different sensors with ZnO layers deposited for different times – 30, 35 and 60 min. The change in the frequency, \(\Delta F\), of the QCM as a function of the loaded mass of NO\textsubscript{2} was detected in different NO\textsubscript{2} concentrations in the range of 250 – 5000 ppm and the value of the sorbed mass was calculated, together with the rate of the NO\textsubscript{2} sorption and desorption. As the time of ZnO layers deposition was increased, the sorbed NO\textsubscript{2} mass increased for all concentrations used in the experiment. This can be explained by changes in the ZnO layers’ structure with the time of deposition.

1. Introduction
ZnO has shown growing potential for applications in new optoelectronic and electronic devices [1-4]. It has high chemical stability, low dielectric constant and high optical transmittance. Additionally, ZnO films doped with different elements have demonstrated sensitivity to different gases [3-5]. As a gas-sensing material, it is one of the earliest discovered and most widely applied gas-sensing oxide materials because of its suitable electrical and chemical properties [6].

The quartz crystal microbalance (QCM) is among the extremely sensitive mass devices [3]. It can be used as a gas sensor [5-7] or a biosensor [8, 9]. The QCM sensor’s properties, as sensitivity, selectivity and time response, are strongly influenced by the sensing film’s properties. These sensors are highly sensitive to mass changes in the presence of the test gas. In the present work, we studied the sensing ability to NO\textsubscript{2} in air of QCMs coated with electrochemically-deposited nanostructured (NS) ZnO films. The sensitivity was estimated by following the frequency-time characteristics (FTCs) of

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the QCM, particularly, its resonance-frequency-shift response, $\Delta F$. The behavior was monitored of three different sensors with ZnO layers deposited for different time - 30, 35 and 60 min.

2. Experimental
We used 16-MHz QCMs made of AT-cut quartz substrates with 60-nm Au electrodes thermally evaporated on both sides of the quartz substrates and a Cr underlayer improving the adhesion of Au to the quartz plate. The diameters of the substrates and electrodes were 8 mm and 4 mm, respectively. The quality of a QCM was characterized by its series resonance frequency ($f_r$), equivalent dynamic resistance ($R_d$) and quality factor ($Q$) [10]. These were the parameters that we measured and controlled before and after modifying the QCMs by depositing thin ZnO nanostructured (NS) layers, thus fabricating gas sensors. The layers were formed electrochemically from a slightly acid aqueous solution of ZnCl$_2$ ($5 \times 10^{-3}$ M) and KCl (0.5 M) with pH 4.0 at 80 °C and $-1000$ mV (vs. SCE) using a three-electrode electrochemical cell [11]. The electrolyte was agitated by a magnetic stirrer. The quartz crystal resonator with a Au electrode was used as a cathode and a spectrally-pure-graphite plate was the anode. The deposition was carried out while controlling the redox potential of the system. The total oxygen content in the solution was controlled by a DO&T meter (Hanna Instruments 9146). The duration of the NS ZnO layers deposition was 30, 35 and 60 minutes. The study of the structural properties of the NS ZnO layers was performed by scanning electron microscopy (SEM) using a Philips 515 SEM apparatus.

The gas-sensing properties of the QCM-NS-ZnO system were investigated at different NO$_2$ concentrations by using an experimental laboratory setup consisting of a gas module, a gas mixing and control module, a test chamber, a thermostat, an oscillator and a frequency counter, and a computer system. The setup was described in detail in [12]. The QCM-NS-ZnO structures investigated were placed in the test chamber near a Pt heat-sensor, so that the temperature of the process was maintained constant and strictly controlled. All samples were measured at the temperature of 24°C ± 0.2°C. The setup was operating in a dynamic mode – in a continuous gas flow. The testing gas consisted of 10 000 ppm NO$_2$ diluted in high-purity synthetic air as a carrier gas. The flow rates of the two gases were measured and controlled by mass flow controllers (FC-260 and FC-280), with the desired NO$_2$ concentration obtained by varying the ratio of the two gas flows. The QCM frequency was registered by a Hamag 8123 frequency counter, and the data was saved on a computer.

The frequency changes as a function of the deposition time (FTCs) for each QCM-NS-ZnO structure were measured at NO$_2$ concentrations ranging from 250 ppm to 5000 ppm. The measurement process can be divided into the following stages:
- with the QCM-NS-ZnO structure placed, the test chamber was purged by the main flow of carrier gas until the frequency reached a constant value;
- the test gas NO$_2$ was included to the main flow; the frequency value decreased due to the loading of the structure. The process continued until a constant frequency value, i.e., saturation, was reached;
- the gas flow was turned off and the frequency started increasing due to unloading of the NS ZnO layers. The process continued until the recovery was complete and the initial frequency was reached.

At this step, the measurements were stopped and the FTC was completed. The sensitivity of the QCM-NS-ZnO system with different NO$_2$ loads was determined by measuring the FTCs. The sorbed NO$_2$ mass ($\Delta m$) was calculated from the QCM resonant frequency-shift measured, in accordance with Sauerbrey’s equation [13].

3. Results and discussion
Figure 1 shows SEM micrographs of NS ZnO layers deposited for 30 and 60 min. The structure consists of planar hexagonal ZnO nano-whiskers with thickness of about 50 – 100 nm in the sample deposited for 30 min, and 200 – 300 nm in that deposited for 60 min, with a height of about 0.5 μm and 1–1.2 μm, respectively. It is seen that the size of the whiskers increases with the electrochemical deposition duration. Increasing the nano-whiskers’ height leads to an increase of the effective surface.
of the NS ZnO layers. The structure of the sample deposited for 35 min is very similar to that of the NS ZnO layer deposited for 30 min.

![SEM micrographs of ZnO nanostructured layers deposited electrochemically on quartz resonators for different time: (a) 30 min, (b) 60 min. The markers correspond to 1 µm.](image)

**Figure 1.** SEM micrographs of ZnO nanostructured layers deposited electrochemically on quartz resonators for different time: (a) 30 min, (b) 60 min. The markers correspond to 1 µm.

Figure 2 demonstrates the change of the frequency (the frequency-shift, $\Delta F$) of the QCM after ZnO layers deposition as a function of the time. After the ZnO deposition, the QCM frequency was reduced by 25.05 kHz, 30.29 kHz and 76.24 kHz for deposition times of 30, 35 and 60 min, respectively. According to Sauerbrey's equation [13], the frequency-shift measured after ZnO deposition is:

$$\Delta F = -\frac{2.26 \times 10^{-6} f^2 \Delta m}{A},$$

where $\Delta F$ is the frequency-shift measured after deposition of NS ZnO layers (Hz), $f$ is the frequency of the QCM before deposition of NS ZnO layers (MHz), $\Delta m$ (g) is the mass of the NS ZnO layers deposited on the QCM surface and $A = 0.1256 \text{ cm}^2$ is the surface area of the electrode.

The deposition mass of ZnO was calculated to be 5.4 µg, 6.7 µg and 16.7 µg, for deposition times of 30, 35 and 60 min, respectively. The other QCM parameters ($R_s, Q$) were also measured and calculated before and after ZnO deposition. After the ZnO deposition, the $R_s$ value increased slightly, while that of $Q$ decreased slightly. This slight deterioration of the QCM parameters did not have a negative influence on the sensors' properties.

Figures 3 (a), (b) and (c) illustrate the FTCs curves of the three QCMs with NS ZnO layers deposited for the three periods of time considered (i.e., with the three different masses of ZnO deposited as quoted above) measured at a 500-ppm concentration of the NO$_2$ test gas. Thus, the time of sorption decreases – 276 s, 252 s and 248 s, as the mass of the NS ZnO films deposited increases, i.e., the rate of sorption increases – 0.123 Hz/s, 0.146 Hz/s and 0.177 Hz/s. The time of desorption at this NO$_2$ concentration increases with the time of ZnO deposition – 104 s, 140 s and 308 s, i.e., the speed of desorption decreases – 0.32 Hz/s, 0.26 Hz/s, 0.14 Hz/s. Or, as it is only to be expected, the mass of ZnO deposited affects the FTCs of the QCMs and the NS ZnO structures’ gas sensing characteristics, since the mass of sorbed NO$_2$ increases with the ZnO mass increase.

Further, we measured the FTCs of QCMs with different mass of NS ZnO films at NO$_2$ concentrations of 250 ppm, 500 ppm, 1000 ppm, 2500 ppm and 5000 ppm. From each FTC, the
frequency-shift was calculated as the difference between the initial frequency value and the frequency value at saturation. Based on the frequency-shift measured, the maximal adsorbed NO$_2$ mass was calculated using the Sauerbrey’s equation.

Figures 4 (a) and (b) illustrate the frequency-shift and the NO$_2$ sorbed mass calculated, respectively, as a function of the NO$_2$ concentration for the QCMs with NS ZnO layers deposited for different times. As seen in the figures, the behavior of the dependences obtained can be divided into two parts regarding the variation of the NO$_2$ concentration, namely, from 250 ppm to 1000 ppm, and from 1000 ppm to 5000 ppm. In the cases of the lower deposition times of NS ZnO layers (30 and 35 min) (lines 1 and 2 in figure 4) and, respectively, of low ZnO mass, the absorption of the gas reaches saturation at about 1000 ppm. In the case of the longest deposition time (60 min), the mass of the NO$_2$ sorbed increases almost linearly with $C_{NO_2}$ up to $C_{NO_2} = 2500$ ppm; at higher $C_{NO_2}$, the frequency, $f$, and the change in $\Delta F$ could not be measured. The changes in the behavior of the QCMs

Figure 3. Frequency-time characteristics of QCMs with NS ZnO layers deposited for different times 30 (a), 35 (b) and 60 (c) min at 500 ppm NO$_2$ concentrations.

Figure 4. Dependences of the frequency-shift, $\Delta F$, (a) and calculated NO$_2$ sorbed mass, $\Delta m$, (b) on the NO$_2$ concentration in the gas flow, $C_{NO_2}$, for QCMs with NS ZnO layers deposited for different time: 1 – 30 min, 2 – 35 min and 3 – 60 min.
sensitivity with the NS ZnO layers deposited for different time is related to the increase of the deposited ZnO mass and of the size of the ZnO nano-whiskers, as seen in the SEM micrographs.

4. Conclusions
We studied the sensing characteristic to NO₂ of 16-MHz QCMs with Au electrodes coated electrochemically by nanostructured ZnO films. The SEM studies revealed that the NS ZnO layers’ surface had developed morphology and high effective surface area consisting of nano-whiskers; the size of the nano-whiskers and the mass of the ZnO grown increased with the time of deposition.

We measured the response and recovery times, the maximal frequency-shift and the mass of gas sorbed on the QCMs with nanostructured ZnO films at different NO₂ concentrations. The QCMs showed good sensitivity to NO₂ at room temperature, making them suitable for detection of NO₂ at concentrations over 250 ppm. The QCM-NS-ZnO system’s sensitivity increased with the ZnO deposition duration, which is explained by the increased ZnO mass and size of the ZnO nano-whiskers, or correspondingly, the increased effective surface area of the NS ZnO layers on a QCM sensor.

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