Application of electrochemically deposited nanostructured ZnO layers on quartz crystal microbalance for NO_2 detection

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Abstract. The research was fixed on sensing behavior of ZnO nanostructured (NS) films to NO_2 concentrations in the environment. The ZnO NS layers are deposited by electrochemical method on quartz resonators with Au electrodes. The sorption properties of ZnO layers were defined by measuring the resonant frequency shift (Δf) of the QCM-ZnO structure for different NO_2 concentrations. The measurements were based on the correlation between the frequency shift of the QCM and additional mass loading (Δm) on the resonator calculated using Sauerbrey equation for the AT-cut quartz plate. Frequency – Time Characteristics (FTCs) of the samples were measured as a function of different NO_2 concentrations in order to define the sorption abilities of ZnO layers. The experiments were carried out on a special set up in a dynamical regime. From FTCs the response and the recovery times of the QCM-ZnO structure were measured with varying NO_2. Frequency shift changed from 23 Hz to 58Hz when NO_2 was varied in the range of 250ppm – 5000ppm. The process of sorption was estimated as reversible and the sorption as physical. The obtained results demonstrated that QCM covered with the electrochemically deposited nanostructured ZnO films can be used as application in NO_2 sensors.

1. Introduction

Nowadays the atmosphere became polluted caused by industrial development and human activity. Ones of the most dangerous gases are the nitrogen oxides (NO, N_2O, N_2O_2, NO_2). The NOx (combination of NO and NO_2) is a typical oxidizing gas, which is found in the combustion exhaust of automobiles and oil-burning power plants. It is acutely toxic and causes problems such as acid rain, photochemical smog and corrosion. This requires monitoring and controlling these gases and development a wide variety of sensors using different materials and technologies [1, 2].

A quartz crystal microbalance (QCM) is one of extremely sensitive mass devices. It is attractive since King firstly introduced it into analytical chemistry [3]. It can be used as gas sensors [4–6], biosensors [7, 8] etc. The QCM sensor properties as sensitivity, selectivity and time response are strongly influenced by the sensing films properties. These sensors are highly sensitive to mass changes

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in the presence of a coating interacting with test gas. The characteristics of QCM gas sensors depend on the materials and the sensing film properties deposited on their electrodes. Many materials have been successfully employed as coatings for QCM sensors [9-11]. ZnO as II–VI semiconductor is one of them. This material posseses high chemical stability, low dielectric constant and high luminous transmittance. As gas sensing material, it is one of the earliest discovered and most widely applied oxide gas sensing material because of its electrcal and chemical properties[12].

ZnO based sensors are sensitive to many sorts of gases, it shows no selectivity for a certain gas. Many attempts are made aimimg to improve its selectivityby using dopants and additives in order to modulate the gas-sensing characteristics [2].

Other approaches for enhancing sensor properties include using the one-dimensional ZnO nanostructures such as nanowires, nanorods, nanobelts and nanotetrapods. They have attracted high attention because of the dimension or surface-to-volume ratio influencing significantlythe material performance [11].

The aim of this study is to investigate NO_2 gas-sensing ability of QCM coated with electrochemically deposited ZnO films towards NO_2 in the air. The sensors characteristics such as response and recovery times, frequency shift and mass-loading of the fabricated structures are studied as a function of different NO_2 concentrations.

2. Experimental

In this work the QCM sensors modified with ZnO nanostructured film are fabricated.

Thin ZnO nanostructured (NS) films are deposited by an electrochemical process from slightly acid aqueous solution of $ZnCl_2$ (5. 10^{-3} M) and KCl (0.5 M) with pH 4.0 at 80ºC and -1000mV (vs SCE) using a three-electrode electrochemical cell [13]. The electrolyte is agitated by magnetic stirrer. The quartz crystal resonator with Au electrode is used as a cathode. Spectrally pure graphite plate electrode is used as an anode. The deposition is carried out controlling the redox potential of the system. The total oxygen content in the solution is controlled by a DO&T meter Hanna Instruments 9146. The duration of the ZnO deposition is 35 minutes. The study of the structural properties of the NS ZnO layer is performed by SEM microscopy using Philips 515 SEM apparatus.

For gas sensing experiments QCM were fabricated on AT-cut quartz substrates. Quartz plates with 8 mm diameter are used. Au-electrodes 4 mm in diameter are thermally evaporated on both sides with a thickness of 60 nm. The Cr underlayer is used for better adhesion of Au electrodes on the quartz plate. The fabricated 16 MHz QCMs are evaluated by measuring the motional resistance (Rs) and calculating the quality factor (Q). These parameters and the series frequency of the QCM loaded with ZnO films are controlled at each stage of the experiments.

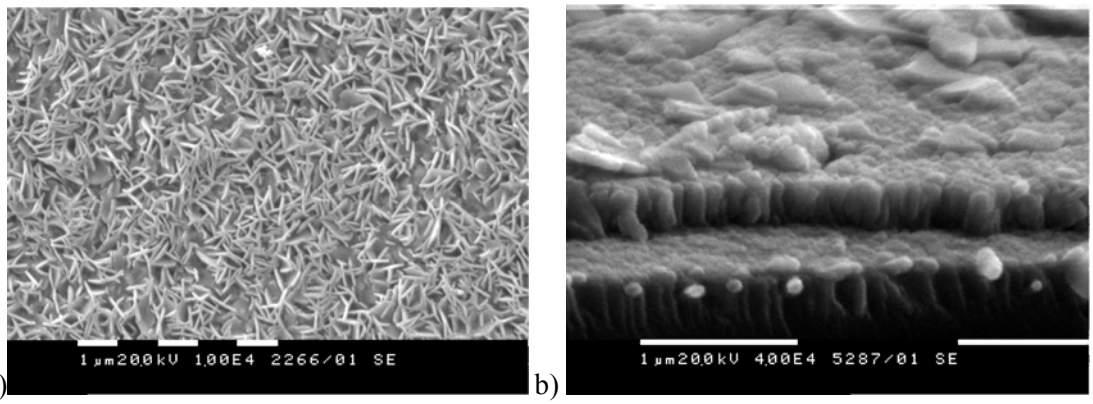
The experimental setup works in a dynamic regime in continuous flow of testing and carrying gases. The sensing properties of the QCM-ZnO to NO_2 are measured by the resonance frequency shift response. The QCM is installed on a special holder inside the test chamber. The temperature of the sample is measured by a Pt-thermosensor placed next to it and is kept constant 24 ± 0.2^0C during the all experiments. The flow rates of the used gases are kept constant by two mass flow controllers (FC-260 and FC-280). Mixing camera provides the homogeneity of the gas mixtures. The ratio of the flows of the test and diluting gases defines NO_2 gas concentration. In the experiments a dry synthetic air – high purity and 10 000 ppm NO_2 diluted in synthetic air are used.

The measurement process consists of three basic stages: purging the camera with air flow until the frequency of the QCM-ZnO reaches a constant value (F_o); switching NO_2 and reaching the saturation frequency value (F); purging the camera with dry air until approaching the initial frequency of the investigated structure. The measurements have been carried out continuously with two seconds interval. A frequency counter Hameg 8123 is connected to the QCM and to the computer for data recording QCM frequency. In this way the frequency change of the QCM-ZnO structure as a function of time is registered for different NO_2 concentrations.

A schematic diagram of the experimental setup and more details of the methodology for the sensing test are presented in Ref [14]. The sensitivity of the QCM-ZnO system to NO_2 is determined by measuring the frequency – time characteristics (FTCs) at different NO_2 concentrations.

3. Results and discussion

Figure 1 shows Scanning Electron Microscopy (SEM) micrographs of ZnO nanostructured thin film, deposited at constant charge density for 35 min. The structure of this thin film consists of planar hexagonal ZnO nano-whiskers (NW) with thickness of about 100-200 nm and different length (0.5-0.8 μm), stacked with the narrow side to the substrate surface. The SEM micrographs reveal the porous surface morphology of the deposited layer.



a) b)

Figure 1. SEM micrographs of ZnO nanostructured layer deposited by electrochemical method on quartz resonator: (a) – surface view and (b) cross section view.The markers correspond to 1 μm.

The quartz resonator parameters measured and calculated are: serial frequency F_s = 15.898964 Hz, equivalent dynamic resistance (R_s) = 7.15Ω, and quality factor (Q) = 55 676. After the electrochemical ZnO deposition, as a result of the loading, F_s decreases with 30.29 kHz, while an insignificant worsening is registered for R_s and the Q to 8,2 Ω and 49193, respectively. After treating the QCM-ZnO system at different NO_2 concentrations, the values of its parameters do not change (8.26 Ω and 48943). This indicates that the QCM-ZnO system is stable after the loading processes and it is fully restored after gas treatments in NO_2 concentrations ranging from 100 ppm to 5000 ppm.

The frequency-time characteristics (FTCs) of the QCM-ZnO system measured at different NO_2 concentrations are presented in figure 2. On the basis of the FTCs, the saturation times reached and the corresponding times for system recovering, i.e. desorption times, are determined. The obtained data from the FTCs are presented in figure 3. With the increase of the NO_2 concentration, the total time ($t_{s\ total}$) for saturation during the sorption process increases from 160 sec to 432 sec for gas concentration range 250 ppm - 5000 ppm, approximately three times (2.7). A similar dependence is established also for the desorption process, at which full desorption is reached. The desorption time ($t_{d\ total}$) arises from 100 sec to 244 sec (2.4 times) in the investigated NO_2 concentration range.

Two areas (fast and slow) are observed in the sorption-desorption zone in all measured FTCs. Compared to the full sorption times, $t_{s\ total}$ (160 sec – 432 sec), these belonging to the fast sorption, t_{s1}, are approximately two times shorter – from 85 sec to 188 sec. Comparison of the times of fast sorption (85 sec- 188 sec) to those of fast desorption, t_{d1}, (25 sec -75 sec) shows that the desorption process is twice faster.

From the resulting FTCs curves in all studied gas concentrations it is assumed that the sorption process has an adsorption-diffusion mechanism. The FTCs also show that the sorption process is reversible for all the measured concentrations.

The FTCs make possible not only the characterization of the process of sorption, but also the determination of the maximal quantity of the substance adsorbed at a fixed NO_2 concentration.

The maximal frequency shift of the system during dynamic equilibrium is illustrated in figure 4.

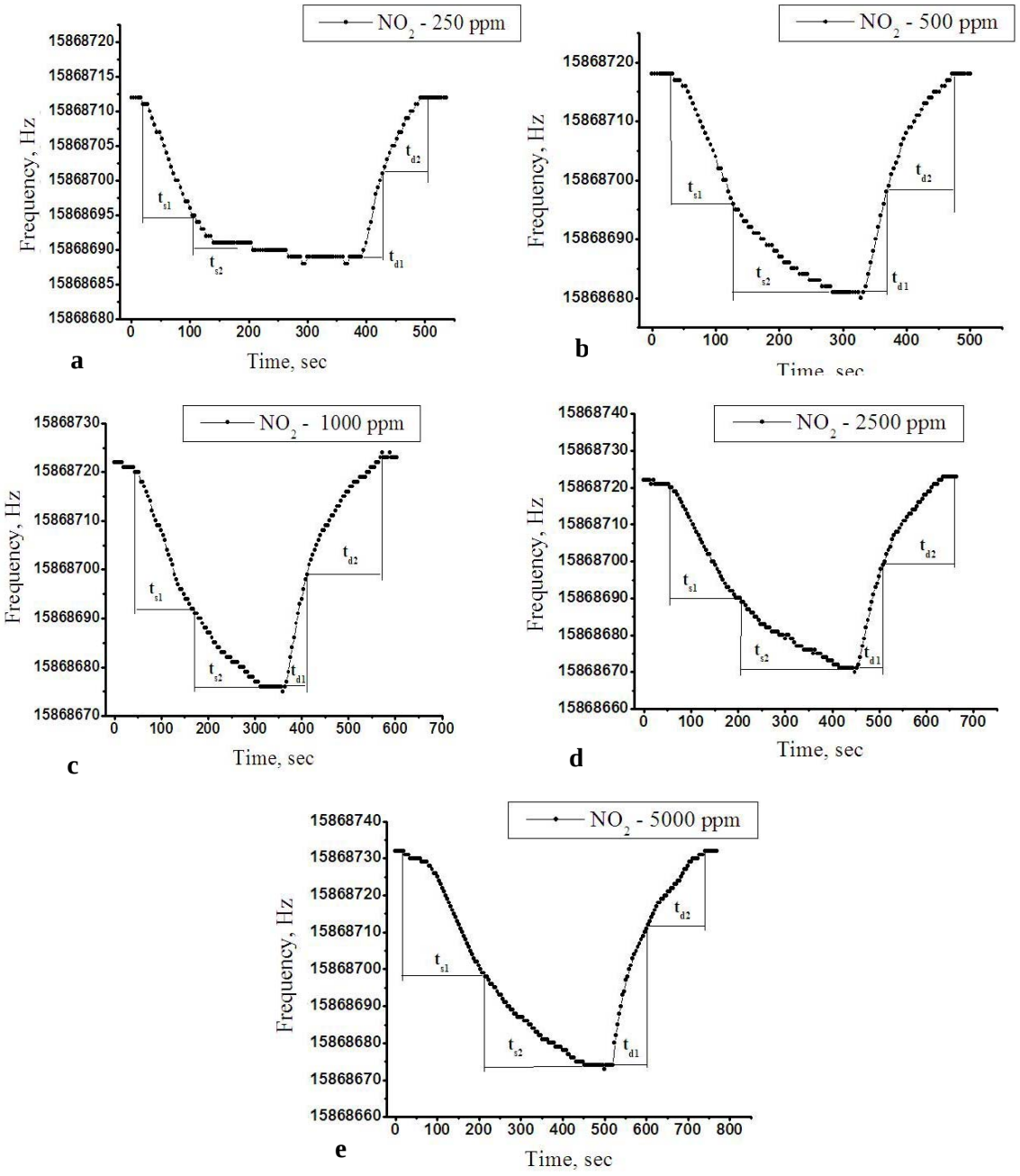


Figure 2 Frequency-time characteristics of QCM with NS ZnO layer at different NO_2 concentrations: a) 250 ppm, b) 500 ppm, c) 1000 ppm, d) 2500 ppm and e) 5000 ppm.

Based on the measured frequency shift, the maximal adsorbed mass is calculated according the Sauerbery equation [15]:

$$\Delta F = -\frac{(2{,}26\times10^{-6}\times f^2\times\Delta m)}{A}, \quad (1)$$

where ΔF is the measured frequency shift for the time reaching the saturation during the NO_2 exposure (Hz), f - is the frequency of the QCM before exposure to NO_2 (MHz), Δm (g) is the mass of the sorbed gas on the surface of the ZnO films and A = 0.1256 cm^2 - is the surface area of the electrode.

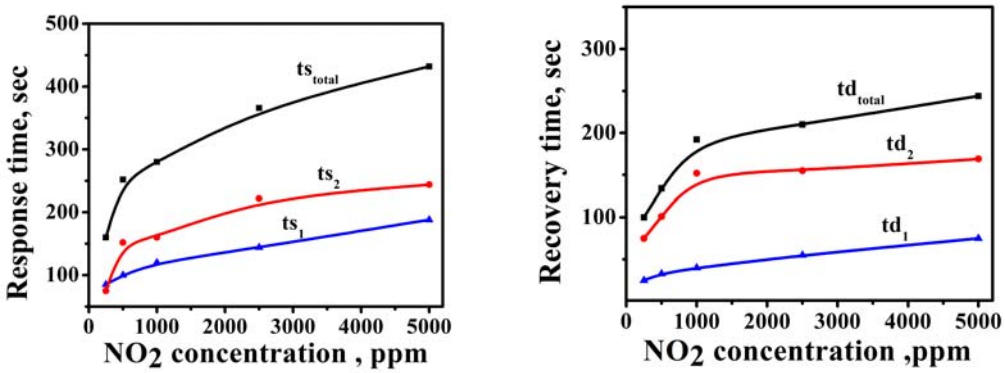


Figure 3. Response and recovery times of QCM-ZnO vs. NO_2 concentration: ts_1 - the time of fast sorption, ts_2 – the time of slow sorption, ts_{tot} = ts_1 + ts_2 - the response time; td_1 - the time of fast desorption, td_2 – the time of slow desorption, td_{tot} = td_1 + td_2 - the recovery time.

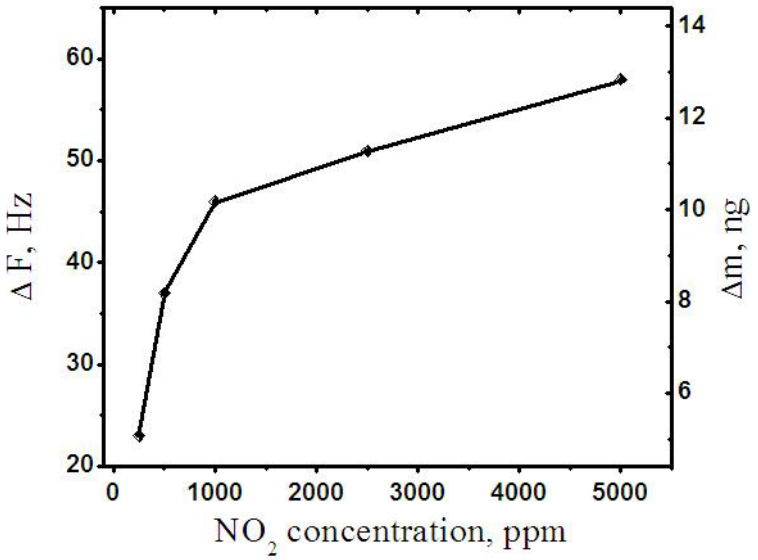


Figure 4. Dependence of QCM-ZnO frequency shift and sorbed mass vs NO_2 concentration.

The obtained dependence is linear for the gas concentration ranging from 250 ppm to 1000 ppm and the change in the frequency shift is from 23 Hz to 58 Hz corresponding to mass change from 5.08 ng to 10.15 ng. The frequency shift values over this concentration decrease significantly, as at 5000 ppm they reach 58 Hz which corresponds to mass of 12,08 ng.

Conclusion

The sensing characteristic to NO_2 of quartz crystal microbalance coated by nanostructured ZnO layer is investigated. The ZnO nanostructured layer is electrochemically grown on Au electrodes of 16 MHz QCM. SEM study reveals that ZnO layer possesses surface consisting of nano-whiskers and has developed surface morphology.

The response and recovery times, maximal frequency shift and sorbed mass at different NO_2 concentrations of QCM with ZnO nanostructured layer are measured. The QCM shows good response to NO_2 at room temperature and can be used for detection of NO_2 concentration higher than 250 ppm. Further more detailed study is required to extend the sensitivity of the system for example by increasing the effective developed surface of ZnO nanostructured layers.

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References

[1] Navale S C, Ravi V, Mulla I S , Gosavi S W and Kulkarni S K 2007 *Sensor Actuat B-Chem* **126** 382
[2] Wagh M S, Jain G H, Patil D R, Patil S A and Patil L A 2006 *Sensor Actuat B-Chem* **115** 128
[3] King W H 1964 *Anal. Chem.* **36** 1735
[4] Sun L-X and Okada T 2000 *Anal. Chim. Acta* **421** 83
[5] Nakamura K, Nakamoto T and Moriizumi T 2000 *Mater. Sci. Eng. C* **12** 3
[6] Zhang J, Hu J Q, Zhu F R, Gong H and O'Shea S J 2002 *Sensor Actuat B-Chem* **87** 159
[7] Bunde R L, Jarv E J and Rosentreter J J 1998 *Talanta* **46** 1223
[8] Guibault G G, Hock B and R. Schmid R 1992 *Biosens. Bioelect.* **7** 411
[9] Gomes M, Nogueira P and Oliveira J 2000 *Sensor Actuat B-Chem* **68** 2000 218
[10] Ding B, Kima J, Miyazaki Y and Shiratori S 2004 *Sensor Actuat B-Chem* **101** 373
[11] Wang X H, Ding Y-F, Zhang J, Zhu Z-Q, You S Z, Chen S-Q and Zhu J, 2006 *Sensor Actuat B-Chem* **115** 421
[12] Seiyama T, Kato A, Fujiishi K and Nagatani M 1962 *Anal. Chem.* **34** 1502
[13] Dimova-Malnovska D, Andreev P, Sendova-Vassileva M, Nichev H and Starbova K 2010 *Energy Procedia* **2** 55
[14] Georgieva V, Stefanov P, Spassov L, Raicheva Z, Atanassov M, Tincheva T, Manolov E and Vergov L 2009 *J. Optoelectr. Adv. Mater.* **11** 1363
[15] Sauerbrey G 1959 *Zeitschrift für Physik* **155** 206