Room-temperature sensitivity to NO₂ exposure of electrochemically-deposited nanostructured ZnO layers

K Lovchinov¹,³, M Petrov¹, M Ganchev¹, V Georgieva², H Nichev¹, B Georgieva¹ and D Dimova-Malinovska¹

¹Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee. 1784 Sofia, Bulgaria
²Acad. G. Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee. 1784 Sofia, Bulgaria

E-mail: lov4@abv.bg

Abstract. This paper reports studies on the sensitivity of ZnO layers to NO₂ exposure. ZnO layers were fabricated by electrochemical deposition on the surface of a quartz crystal microbalance (QCM) with Au electrodes. The sensitivity was estimated using the frequency-time characteristics of the QCM. For this purpose, the resonance frequency shift was measured. The sorption process was investigated in a NO₂ gas flow. The change in the resonance frequency, \( f \), of the QCM as a function of the loaded mass of NO₂ was followed for a NO₂ concentration of 500 ppm. Under gas exposure, the frequency decreased and reached saturation in five min. A frequency shift of 38 Hz was measured and a mass loading of 8.39 ng was calculated. The resonance frequency showed a very good recovery within two minutes after the NO₂ flow was switched off. The results demonstrate that the electrodeposited nanostructured ZnO layers have a potential for application as NO₂ gas sensors.

1. Introduction
Recently, TCO materials, and especially ZnO, have shown a growing potential for applications in the development of new optoelectronic and electronic devices. Having a high chemical stability, a low dielectric constant and a high optical transmittance, ZnO has found numerous uses as dielectric ceramics, pigment, catalyst, transparent conductive electrode and sensing material in solar cells, gas sensors, etc. [1-4]. In particular, an increase in the gas sensitivity and selectivity for different gases has been reported by doping ZnO films with different elements [3-5].

In this work, the sensitivity of undoped thin films of ZnO to exposure to NO₂ was estimated by means of the quartz crystal microbalance (QCM) method.

2. Experimental
Thin ZnO nanostructured films were deposited by an electrochemical process from a slightly acidic aqueous solution of ZnCl₂ (5×10⁻³ M) and KCl (0.5 M) with pH 4.0 at 80 °C and −1000 mV (vs. SCE) using a three-electrode electrochemical cell [6]. The electrolyte was agitated by magnetic stirrer. The quartz crystal resonator with a Au electrode was used as a cathode. A spectrally-pure graphite plate

³ To whom any correspondence should be addressed.
electrode was used as an anode. The deposition was carried out for between 30 and 60 minutes while controlling the redox potential of the system. In addition, the total oxygen content in the solution was controlled by a DO&T meter (Hanna Instruments 9146). The thickness of the ZnO films thus prepared was in the range 0.2 µm − 0.5 µm.

Quartz crystal resonators were used as microbalances to monitor the speed of electrodeposition of the ZnO nano-layers. The oscillators consisted of thermo-stable polished AT-cut quartz plates with a diameter of 8 mm with gold electrodes with a thickness of 600 nm and a surface area of 0.1256 cm² in an HC-49 type package. A 16-MHz base resonance frequency was thus obtained.

The gas sensitivity of the electrochemically-deposited ZnO on QCM was studied by exposure to NO₂. The resulting structure was kept in air until saturation in the frequency value was reached. The temperature in the test chamber was kept constant (25 °C ± 0.5 °C) by a thermostat. The concentration of the NO₂ gas flowing into the thermally-stabilized measurement chamber was 500 ppm. The resonance frequency was measured by a frequency counter and recorded on a PC. The experimental setup for measuring the sensing properties of the ZnO-QCM system was described in detail in [7]. The frequency accuracy was ~ 0.1 Hz.

3. Results and discussion

To determine the films’ growth rate, several experiments were performed involving deposition of ZnO on a quartz resonator surface, the ZnO layers being deposited for four different time durations – 30, 35, 45 and 60 min. Figure 1 shows the dependence of the ZnO films’ thickness on the deposition time. The layers’ thickness was calculated from the change in the resonance frequency caused by the ZnO film deposited using the Sauerbrey equation [8]. The dependence could be fit by a straight line:

\[ d = 0.01123t - 0.17837, \]  

where \( d \) is the Sauerbrey thickness of the layer (in nm) and \( t \) is the plating time (in minutes).

The slope of the line yields a value of the film growth rate of 11 nm/min. The negative term of equation (1) indicates a delay in the film growth onset (nucleation time), whose value (at \( d = 0 \)) is about 15 min [9].

Figure 2 shows a scanning electron microscopy (SEM) micrograph of a nanostructured ZnO thin film deposited at constant charge density for 60 min. The structure of this thin film consists of planar hexagonal ZnO nano-whiskers (NW) with a thickness of about 100 − 300 nm and different lengths (0.5 − 1 µm), stacked with the narrow side to the substrate surface. The thickness of the ZnO film is 0.5 µm. The SEM micrograph reveals the porous surface morphology of the deposited layer.
The ability of the ZnO thin films to sorb NO2 was evaluated by the QCM method. For this purpose, the resonance frequency shift was measured. The sorption process was investigated in a gas flow of NO2 with a concentration of 500 ppm by following the change in the frequency, \( f \), of the QCM as a function of the mass loading. Figure 3 shows this change as a function of the exposure time. The highest rate of frequency change, \( S_p = 11.5 \text{ Hz/min} \), was registered in the first two minutes. After that, the rate decreased more slowly, with the frequency reaching a constant value within about five minutes after exposure to NO2. When the gas flow was switched off, the frequency returned to its initial value within two minutes due to the desorption of the gas, the fastest change occurring in the first minute. The rate of change was calculated for the first five minutes after exposure to the NO2 in order to estimate the sensitivity of the electrodeposited ZnO layer. The average value of the frequency-change rate, \( S_p \), and of the total sorbed mass, \( \Delta m \), were evaluated on the basis of the time-frequency characteristics measured using the relationship between \( \Delta f \) and \( \Delta m \) for AT-cut quartz plates as given by the Sauerbrey equation [6, 8]:

\[
\Delta f = -\left(2.6\times10^6 f^2 \Delta m\right)/A,
\]

where \( f \) (MHz) is the frequency of the QCM before exposure to NO2, \( \Delta m \) (g) is the mass of the gas sorbed on the surface of the ZnO films, and \( A \) (cm\(^2\)) is the surface area of the Au electrodes. In our experiments, the frequency shift measured, \( \Delta f \), was 38 Hz, and the sorbed mass, \( \Delta m \), was calculated to be 8.39 ng. The \( S_p \) value of 7.6 Hz/min was calculated as the ratio of the frequency shift to the time of saturation (five minutes).

The electrochemically-deposited ZnO layer with grown nano-whiskers had a highly developed surface interacting with the NO2 molecules. When the concentration of the gas in the chamber is raised, the NO2 molecules are adsorbed in the ZnO layer; as a result, the resonator’s mass increases and its frequency decreases. When the gas flow in the chamber is stopped, the NO2 molecules start desorbing and the frequency of the quartz resonator returns to its initial value.

4. Conclusions

The sensing characteristic to NO2 of nanostructured ZnO layer electrochemically deposited on the surface of a QCM was studied. The structure of the ZnO layer, as revealed by SEM, consisted of nano-whiskers and had a developed surface morphology. The NO2 mass sorbed in the ZnO layer at room temperature and 500 ppm concentration of the gas flow was calculated from the change in the frequency of the QCM after exposure to NO2. The change in the frequency reached saturation within five minutes after exposure to the NO2 flow; the absorbed mass was calculated to be 8.39 ng. The time of frequency recovering once the gas flow is switched off was high – about 2 minutes. The results obtained demonstrated a potential application of the electrochemically-deposited nanostructured ZnO layers as room-temperature gas sensors of NO2.

Acknowledgement

The work was funded under the 7 European FP – project NanoPV No. 24331
References
[1] Dimova-Malinovska D, Tzenov N, Tzolov M and Vassilev L 1998 J. Mater. Sci. Technol. B 52 59
[2] Cao Y, Miao L, Tanemura S, Tanemura M, Kuno Y, Hayashi Y and Mori Y 2006 Jap. J. Appl. Phys. 45 1623
[3] Rao G S T and Rao D T 1999 Sensors Actuators B 55 166
[4] Aslam M, Chaudhary V, Mulla I, Sainkar S, Mandale B, Belhekar A and Vijayamohanan V 1999 Sensors Actuator 75 162
[5] Koshizaki N and Oyama T 2000 Sensors Actuators B 66 119
[6] Dimova-Malinovska D, Nichev H, Georgieva V, Angelov O, Pivin J C and Mikly V 2008 Phys. Status Solidi A 205 1993-7
[7] Georgieva V, Stefanov P, Spassov L, Raicheva Z, Atanassov M and Tincheva T 2009 J. Optoelectr. Adv. Mater. 11 1363
[8] Sauerbrey G 1959 Zeitschrift für Physik 155 206
[9] Lovchinov K, Ganchev M, Petrov M, Nichev H, Rachkova A, Angelov O, Mikli V and Dimova-Malinovska D 2013 Phys. Status Solidi A 210 743-7