

## Effect of quartz plate roughness on ZnO/QCM response to NO<sub>2</sub>

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The influence of the quartz roughness on the ZnO sorption properties is investigated. AT-cut quartz plates with differently treated surface - flat polished and unpolished ones are used. The nanostructured ZnO layers are deposited by electrochemical method on the Au electrodes of the quartz crystal micro-balances resonators (QCM). Thin ZnO nanostructured films are deposited by an electrochemical process from slightly acid aqueous solution of ZnCl<sub>2</sub> (5 · 10<sup>-3</sup> M) and KCl (0.5 M) with pH 4.0 at 80°C and -1000mV (vs SCE) using a three-electrode electrochemical cell. The structure of the ZnO layers deposited on the polished and unpolished QCM surface is studied by SEM, AFM and the optical spectroscopy - by the spectra of specular and diffused reflection. The results are compared to the corresponding data obtained for the QCM before ZnO growing. The sorption ability of the ZnO thin layers is defined by measuring the resonant frequency shift ( $\Delta f$ ) of the QCM-ZnO structure in the presence of different NO<sub>2</sub> concentration (50 - 5000 ppm). The correlation between the sorption ability of the ZnO and the different state of the quartz surface is obtained from the QCM response. The QCM with ZnO deposited on the polished quartz demonstrate better sorption ability compared to QCM fabricated on unpolished quartz surface.

**Key words:** ZnO, nanostructure, electrochemical deposition, quartz microbalance resonator, gas sensors.

### INTRODUCTION

The quartz crystal microbalance (QCM) is one of the extremely sensitive mass detection devices. It is widely used such as gas sensors, biosensors, etc. The QCM sensor properties such as sensitivity, selectivity, and time response are strongly influenced by the properties of the sensing films. These sensors are highly sensitive to mass changes in the presence of a coating, which interacts with the test gas. The characteristics of QCM gas sensors depend on the kind and structure of sensing films coated on their electrodes. A number of materials have been successfully employed in the coating of QCM sensors and one of them is ZnO, II–VI semiconductor. This material possesses 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 gases sensing material because of its optical, electronic, and chemical properties [1, 2-5].

In this paper results from investigation of the optical and the structural properties of nanostructured ZnO thin films formed by

electrochemical deposition on two Quartz Crystal Microbalance (QCM) resonators with differently treated surface – polished and unpolished are presented. The sensitivity of both QCMs to NO<sub>2</sub> is compared and the influence of the roughness of the quartz substrate on ZnO sorption properties of two QCM is investigated.

Electrodeposition has some advantages as a method of deposition because it is a low cost industrially up-scalable process, relevant to different substrates for preparation of well defined nanostructures with reasonable physical parameters [2, 3, 6].

### EXPERIMENTAL

The nanostructured ZnO layers are deposited by electrochemical method on the Au electrodes of the QCM resonators. Thin ZnO nanostructured films are deposited from slightly acid aqueous solution of ZnCl<sub>2</sub> (5 · 10<sup>-3</sup> M) and KCl (0.5 M) with pH 4.0 at 80°C and -1000mV (vs SCE) using a three-electrode electrochemical cell [7,8]. The electrolyte is agitated by magnetic stirrer. The Au electrode of the QCM 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 WENKING HP 96. The total

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oxygen content in solution is controlled by a DO&T meter Hanna Instruments 9146. Duration of the ZnO deposition is 60 min. The thicknesses of the prepared ZnO films are in the range of 0.5-0.7  $\mu\text{m}$ .

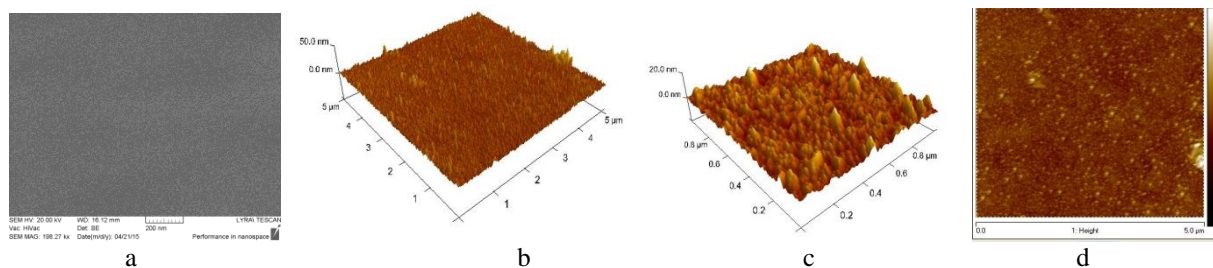
The morphology of the obtained ZnO layers is characterized by Scanned Electron Microscopy (SEM) (microscope Lyra (Tescan) with Secondary Electron and Back Scattering Electron detector and EDX detector Quantax 200 (Bruker) and AFM (Multimode V -Veeco) in tapping mode and height, amplitude and phase images are recorded. The optical properties - spectra of specular reflectance, diffuse reflection and haze ratio in reflection are measured by a spectrophotometer Shimadzu UV-3600 in the range 330 -1200 nm employing a 60 mm integrating sphere. The sorption ability of the ZnO thin layers is defined by measuring the resonant frequency shift ( $\Delta f$ ) of the QCM-ZnO structure in the presence of different  $\text{NO}_2$  concentrations (50 - 5000 ppm). The experimental setup works in a dynamic regime in continuous flow of testing and carrying gases. The QCM is installed on a special holder inside the test chamber. The flow rates of the used gases are measured inside the test chamber by a Pt-thermo-sensor placed next to it and is kept constant  $24 \pm 0.2^\circ\text{C}$  during the 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  $\text{NO}_2$  gas concentration. In the experiments a dry synthetic air

– high purity and 10 000 ppm  $\text{NO}_2$  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; switching  $\text{NO}_2$  and reaching the saturation frequency value; purging the camera with dry air until approaching the initial frequency of the investigated structure. The measurements have been carried out continuously at 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  $\text{NO}_2$  concentrations.

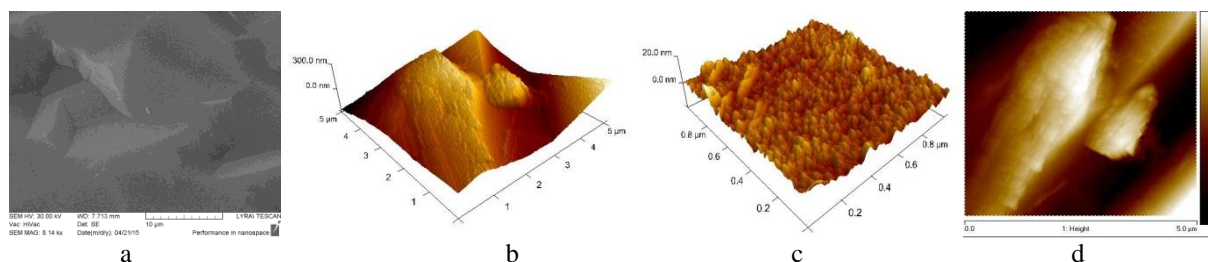
## RESULTS AND DISCUSSION

The surface morphology of the polished and unpolished quartz substrates studied by SEM and AFM before ZnO layers coating are shown in figure 1 and 2, respectively. The surface of polished QCM with deposited Au electrode is very flat (figure 1 a) and the value of the average surface roughness is  $R_{\text{avr}} = 7.45 \text{ nm}$  and of the maximal roughness  $R_{\text{max}} = 34.9 \text{ nm}$  (figure 1 b and c).

The surface of the unpolished QCM is very rough – the plates and pyramidal like structures with size of several  $\mu\text{m}$  and different high (between about 2 and  $8 \mu\text{m}$ ) are seen in the SEM image (figure 2a). The surface roughness is  $246 \text{ nm}$  and the maximal roughness is  $461 \text{ nm}$  (figures 2 b and c).



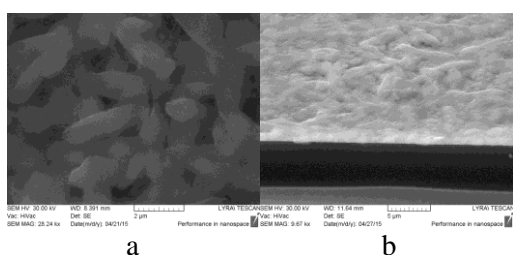
**Fig. 1.** SEM micrographs (a) and AFM pictures (b,c,d) of the polished quartz substrate with  $R_{\text{avr}} = 7,45 \text{ nm}$  and  $R_{\text{max}} = 34,9 \text{ nm}$  (d). The marker in (a) corresponds to 200 nm.



**Fig. 2.** SEM micrographs (a) and AFM pictures (b,c,d) of unpolished quartz substrate with  $R_{\text{avr}} = 246 \text{ nm}$  and  $R_{\text{max}} = 461 \text{ nm}$  (d). The marker in (a) corresponds to 10  $\mu\text{m}$ .

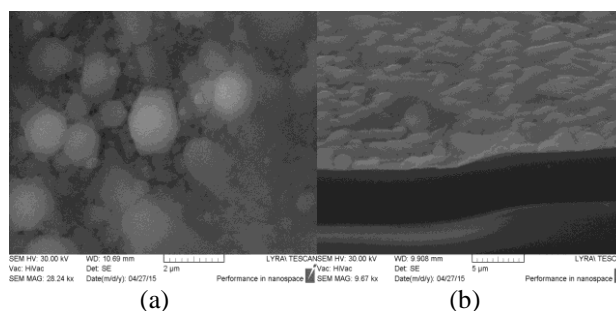
The SEM pictures of the deposited ZnO layers on the polished surface of QCM are shown in figure 3 a and b. The ZnO layer consists of hexagonal nanowires about 700-800 nm thick grown with different orientation to the surface.

In the case of growing on unpolished QCM surface (SEM are shown in figures 4 a and b) the ZnO nanowires with different size – diameter (from 200 nm to 1,5µm) and height have grown perpendicular to the substrate surface. The difference in the height of the ZnO nanowires probably is due to the growing on electrode deposited on the quartz plates with different height. The substrate with higher surface roughness induces the ZnO nanowire growing with higher inhomogeneity in the surface morphology.

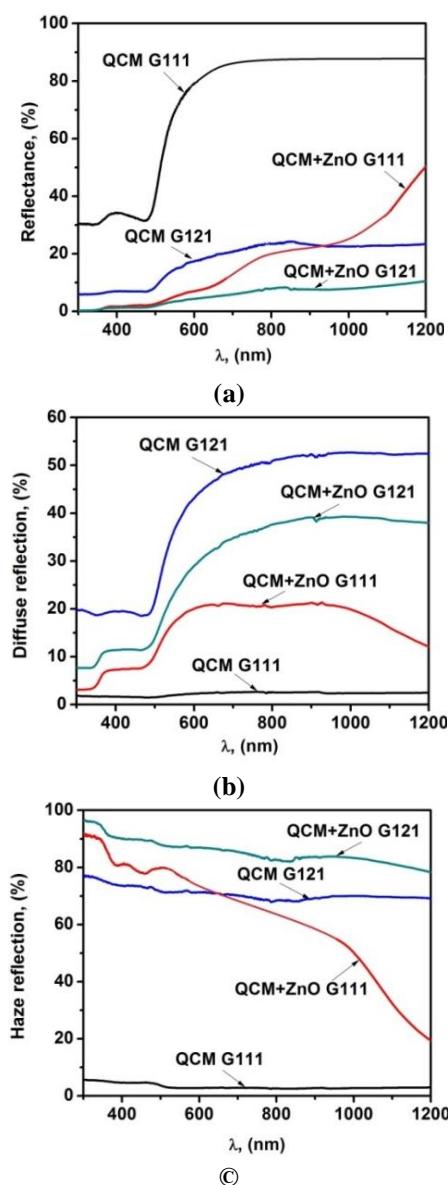


**Fig. 3.** SEM of ZnO nanostructured layer deposited by electrochemical method on polished quartz substrate of QCM resonator (G 111): (a) – surface view and (b) - cross section view. The markers correspond to 1 µm.

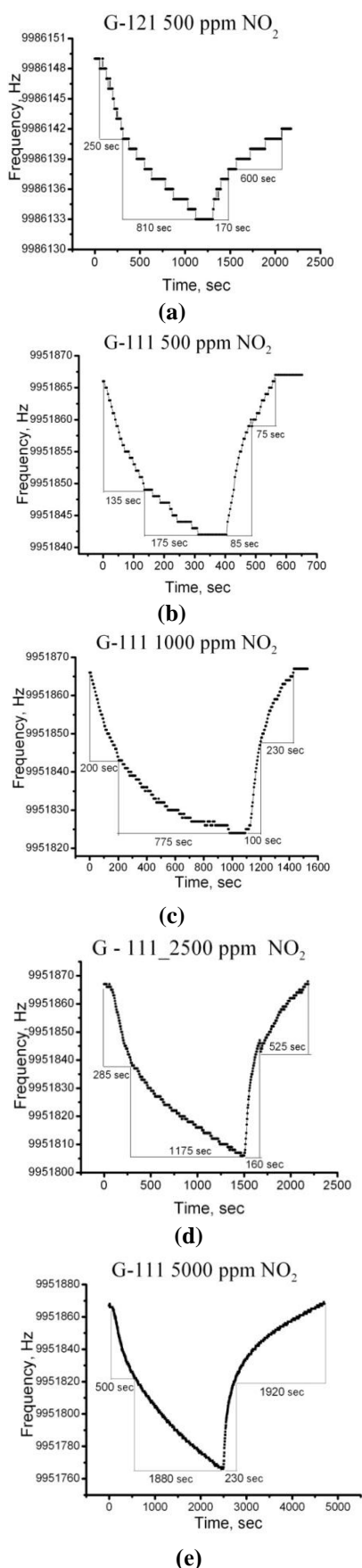
Figure 5 shows spectra of specular reflection, diffuse reflection and haze ratio in reflection of ZnO layers deposited on polished and unpolished QCM substrate. For comparison the corresponding spectra of the QCM before ZnO growing are presented as well. The polished substrate has high values of reflection, low value of diffused reflection and of haze ratio in reflectance. In opposite, the unpolished QCM surface demonstrated low specular reflection, high diffused reflection, and haze in reflectance. After ZnO deposition on polished QCM surface, the reflectance decreases, the diffuse reflection and haze in reflectance increase. In the case of growing on unpolished QCM surface the presence of ZnO nanowires (NW) leads to slight decreasing of the specular reflection, decreasing of diffused reflection and slightly increasing in haze of reflection. It has to be noticed that values of the specular reflection decrease from 70% to 20% after ZnO layer deposition on QCM with polished substrate while these values after ZnO growing on the rough quartz surface of QCM decrease slightly - from 20% to 10% (figure 5a). The changes in the values of reflection are due to the increased surface inhomogeneity after ZnO NW growing, more pronounced in the case of growing on polished QCM surface.



**Fig. 4.** SEM of ZnO nanostructured layer deposited by electrochemical method on unpolished quartz substrate of QCM resonator (G 121): (a) – surface view and (b) - cross section view. The markers correspond to 1 µm.



**Fig. 5.** Spectra of specular reflectance (a), diffused reflection (b) and haze ratio in reflection (c) from the ZnO deposited on polished QCM (G 111) and unpolished surface of QCM (G 121).



**Fig. 6.** Frequency – time characteristics of QCM with NS ZnO layer at different NO<sub>2</sub> concentrations: (a) QCM G-121 (unpolished) and (b) QCM G-111 (polished) - 500 ppm; c) 1000 ppm; d) 2500 ppm; e) 5000 ppm.

The process of sorption of NO<sub>2</sub> is compared for two kinds of QCM layers fabricated on different differently treated quartz surface – polished and unpolished at NO<sub>2</sub> concentration for 500 ppm (figures 6 a and 6 b). The QCM with ZnO nanostructured formed on polished quartz surface demonstrates that the process of sorption is reversible in the time of 150 sec. However in the case of the QCM formed on the unpolished quartz surface the value of half of initial frequency is notreached for the time as long as 770 sec. Thedifference in the behavior of two types of QCMs under investigation could be explained by the differences in the structure and morphology of ZnO layers formed on different surfaces. The Zn layer on polished quartz has hexagonal nano-rods with size of 500 nm grown in different angles to the substrate. The ZnO layer grown on the rough quartz surface (QCM G-121) has hexagonal rods with larger size - 2 μm with perpendicular orientation to the substrate.

The higher gas sensitivity of the QCM G-111 compared to QCM G-121 can be explained by the lower size of the grown ZnO rods which results in larger effective surface area. Additionally, it is possible to suppose that the difference in the crystalline orientation of the ZnO rods is a reason for the different sensitivity of QCM. The different crystalline planes of ZnO have different surface defects which are responsible for the gas absorption and this could reflect in different sensibility of the sensors.

The frequency-time characteristics at different NO<sub>2</sub> concentrations are measured for the QCM-111 which demonstrates reversible process of NO<sub>2</sub> sorption. The frequency-time characteristics (figure 6) show that both, the process of sorption and desorption of the NO<sub>2</sub> consist of twosteps: quick and slow ones.

The time of both processes is determined for each value of NO<sub>2</sub> concentration applied. The values of the time of sorption and desorption are shown in figure 6 and summarized in table 1. The results demonstrate that time of the process of quick sorption ( $t_{s1}$ ) rises about 4 times and the time of the slow sorption ( $t_{s2}$ ) – about 11 times with increasing the NO<sub>2</sub> concentration from 500 ppm to 5000 ppm. The total time for reaching the dynamic equilibrium of the process of absorption rises about 8 times. Similar tendency is observed for the process of desorption – the time of the process of initial desorption ( $t_{d1}$ ) increases about 3 times and that of final step of desorption ( $t_{d2}$ ) - about 25 times. It is measured that the total desorption time increases about 13 times with increasing of the NO<sub>2</sub> concentration.

The comparison of the frequency shifts of both QCMs (G-111 and G-121) obtained as a function of NO<sub>2</sub> concentration is shown in figure 8. It is seen that the QCM G-111 with ZnO grown on polished quartz substrate demonstrates higher sensitivity for all values of NO<sub>2</sub> concentrations under investigation.

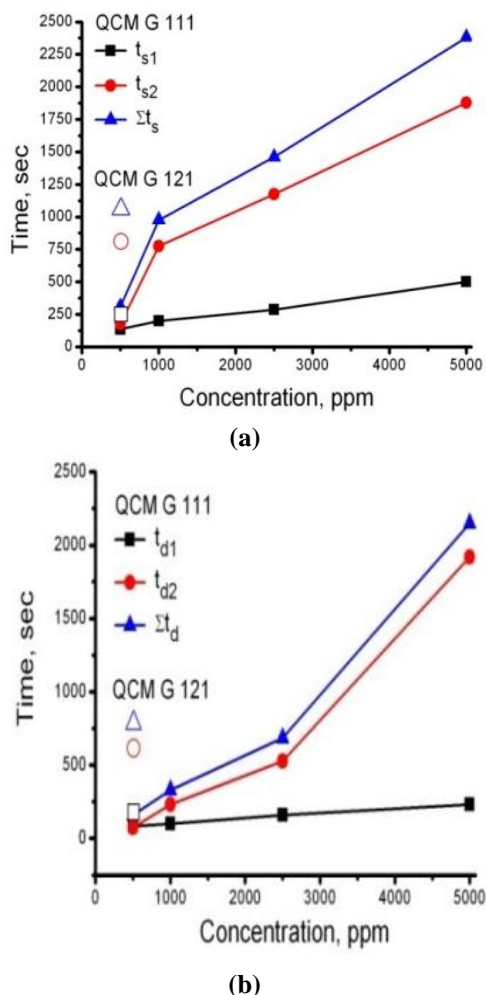


Fig. 7. Dependence of the QCM-ZnO time of sorption,  $t_s$ , (a) and desorption,  $t_d$ , (b) vs. NO<sub>2</sub> concentration.

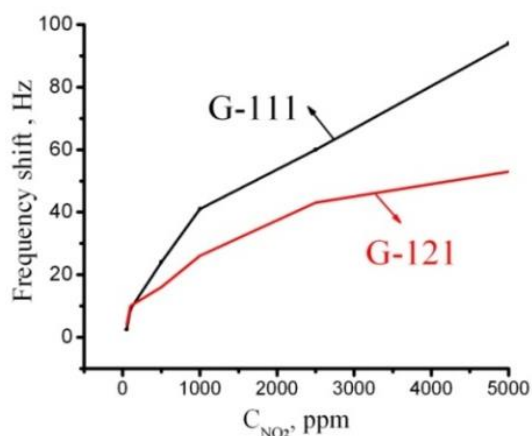


Fig. 8. Dependence of QCM-ZnO frequency shift vs NO<sub>2</sub> concentration.

Table 1. The values of the times of the processes of the quick and slow sorption and desorption by QCMs and the corresponding total times.

Sample	C <sub>NO<sub>2</sub></sub> ppm	Time, sec					
		t <sub>s1</sub>	t <sub>s2</sub>	Σ t <sub>s</sub>	t <sub>d1</sub>	t <sub>d2</sub>	Σ t <sub>d</sub>
QCM G 111	500	135	175	310	85	75	160
	1000	200	775	975	100	230	330
	2500	285	1175	1460	160	525	685
QCM G 121	500	500	1880	2380	230	1920	2150
	500	250	810	1060	170	600	770

### CONCLUSIONS

The ZnO nanostructured layers with developed surface morphology are electrochemically deposited on Au electrodes of QCM on polished and unpolished quartz plate. The surface morphology on the grown ZnO depends on the roughness of the quartz substrate of QCM. The values of reflectance decrease more pronounced after deposition of ZnO on polished quartz surface. The response, maximal frequency shift and recovery times of the processes of sorption and desorption at different NO<sub>2</sub> concentrations between 500 and 5000 ppm of QCMs are measured at room temperature. The QCM formed on polished quartz surface shows good response to NO<sub>2</sub>, higher sensitivity that QCM on the rough quartz substrate and the process of sorption is reversible. The electrochemically deposited nanostructured ZnO layer grown on QCM on polished quartz surface can be used for detection of NO<sub>2</sub>.

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## ВЛИЯНИЕ НА ПОВЪРХНОСТНАТА ГРАПАВОСТ НА КВАРЦОВИ ПОДЛОЖКИ ВЪРХУ СОРБЦИОННИТЕ СВОЙСТВА НА ZnO/QCM КЪМ NO<sub>2</sub>

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(Резюме)

В настоящата работа са представени резултати от изследване на влиянието на повърхностната грапавост на кварцови подложки, използвани в кварцови микро-резонатори (QCM), върху сорбционните свойства на отложени върху тях слоеве от ZnO. Използвани са кварцови пластини с АТ-срез с различна повърхостна морфология – с полирана и неполирана повърхност. ZnO слоеве с наноструктура са отложени чрез електрохимичен процес върху Au електрод на QCM в слабокисел разтвор на ZnCl<sub>2</sub> ( $5 \cdot 10^{-3}$  M) и KCl (0.5 M) с рН=4.0 при 80°C и 1000 mV (vs SCE), използвайки три-електродна система. Структурата на отложените ZnO слоеве върху двата вида повърхности на QCM е изследвана чрез SEM и AFM, а оптичните свойства – от спектрите на директно и дифузно отражение. Резултатите са сравнени със съответните данни, получени за QCM преди отлагането на ZnO. Сорбционните свойства на ZnO слоевете са охарактеризирани чрез измерване на промяната на резонансната честота ( $\Delta f$ ) на QCM-ZnO при различни концентрации NO<sub>2</sub> (50 - 5000 ppm) в газовия поток. Показана е корелация между сорбционна способност на ZnO, отложен върху кварцовите подложки с различна повърхостна морфология. Кварцовият микро-резонатор с ZnO, отложен върху полирана кварцова повърхност, показва по-добра сорбционна способност в сравнение с QCM с ZnO, отложен върху неполирана повърхостна кварцовата подложка.