Quartz roughness affect on WO$_3$ coated QCM

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Abstract. The influence of the initial quartz roughness on the WO$_3$-QCM (Quartz Crystal Microbalance) parameters and sorption properties was investigated. Experiments were carried out using AT-cut quartz crystal with different surface roughness obtained after treatment with SiC abrasive having grain size of 3 μm, 7 μm, 14 μm and 20 μm respectively. The QCMs were covered with thin WO$_3$ films. The equivalent dynamic parameters of the WO$_3$- QCM were measured and a correlation with the surface roughness was determined. The equivalent dynamic resistance of the as–created QCM increases from 15.42 Ω to 117 Ω and the quality factor decreases as a result of the roughness changes. The surface morphology was observed by a Scanning Electron Microscopy (SEM), which showed higher increase of the WO$_3$ surface roughness compared to those of the initial quartz surface. The cross-section profiles of the investigated structures show different overlay of Au-electrodes. The sorption properties of WO$_3$-QCM system to NH$_3$ were studied in the range from 10 ppm to 1000 ppm. The response and recovering times were determined. The experimental results show an increase of the sorption ability with the increase of the initial quartz roughness. By increasing the roughness the mass-loading is improved.

1. Introduction

The adsorption properties of the gas sensing layers depend on the surface morphology. If they are nanostructured of significant importance is the particles’ size, packing of nanoparticles etc. The adsorption properties of sensitive films formed by gold nanoparticles with different content are investigated using mass-sensitive (QCM) sensors [1]. It was established that the change of the surface concentration of nanoparticles leads to change of the sensors’ sensitivity to different alcohols. Another way for enhancing the adsorption is formation of self-assembled monolayer (SAM) on the surface of gold QCM electrode. Such investigation was carried out by Kim and coworkers [2], who found that a circular and strip type structures of SAM show extremely high adsorption to the octadecanethiol solutions in hexane and alcohol, compared to the smooth surfaces. Mérian et al. have investigated the ammonia absorption properties of polyaniline [3]. The results show that the oxidative doping is very efficient to obtain a highly adsorbing and sensitive layer. The adsorption properties of several IrO$_2$ layers with different morphologies, such as nanoblade, layered-column, incomplete-nanotube and square-nanorod have been studied [4]. IrO$_2$ crystals with nanoblade and layered-column morphologies...
show higher sensitivities than those with incomplete-nanotube and square-nanorod morphologies. By replace of the conventional gold electrodes with porous Hieda et al. have found that the effective adsorbing surface area and hence sensitivity was enhanced by a factor of 40 without worsen of the quality factor or the stability of the resonant frequency [5]. WO$_3$ nanoflake functionalized QCM sensors were fabricated for detection of trace sarin stimulant and dimethyl methylphosphonate [6]. The sensors have better reproducibility and stability as well as much shorter response and recovery time than those functionalized by conventional flat WO$_3$ surface. Faster response has also been observed for ZnO functionalized QCM sensors for detection of ammonia [7]. In the recent years, one-dimensional ZnO nanostructures, such as nanowire, nanorods, nanobelts, and nanotetrapod, have been attracted much attention since the dimension or the surface-to-volume ratio has great influence on the performance [8]. In this work the influence of the initial quartz surface roughness, obtained by different grain size abrasive on the WO$_3$ roughness, WO$_3$-QCM equivalent parameters and sorption properties to NH$_3$ is studied.

2. Experimental

For the purpose of the present work, quartz plates with different surfaces were processed by using SiC abrasive with grain size of 3 μm, 7 μm, 14 μm and 20 μm. Samples of polished quartz plates were fabricated too. QCMs were formed on AT-cut quartz plates with diameter of 8 mm. Au-electrodes with 4 mm diameters and thickness of 60 nm were evaporated on both sides. Thus, QCMs with resonance frequency of 16 MHz were fabricated. QCM’s quality was evaluated by measuring the main equivalent dynamic parameter - dynamic resistance ($R_q$), by a Selective Level Meter, the other parameters such as quality factor (Q), were calculated [9]. The created structures were coated with a WO$_3$ layer deposited by RF sputtering at 13.56 MHz from W target in (Ar + O$_2$) mixture containing 50% O$_2$. The process was carried out at a total pressure ($P_Ar$ + $P_O2$) of 4.10$^{-2}$ mbar and deposition rate of about 19.5 nm/min. The refractive index and thickness of the WO$_3$ films were determined by ellipsometric measurements on control silicon wafer, placed next to the resonator structure. A Rudolph 435 ellipsometer of 632.8 nm was used. The surface morphology of the WO$_3$ films deposited on the resonators was determined using a SEM-Philips 515. The samples were covered additionally with C and Au thin layers in order to increase the resolution and because of avoiding the charge. The cross-section profiles of all samples were studied too. The sorption abilities of the WO$_3$ films were determined by measuring the resonance frequency shift of QCM at different NH$_3$ concentrations. The frequency-time characteristics (FTCs) for all samples were measured. The sorption properties of the WO$_3$-QCMs to NH$_3$ are measured in laboratory set up. The experimental unit and the methodology of measurements are described in details in [10]. The main stages of the measurement consisted of:

- purging of the structures with dry air;
- creating a certain NH$_3$ concentration;
- reaching saturation of the frequency values;
- purging of the structures with dry air.

The NH$_3$ concentration in the test chamber was controlled by mass flow controllers (MFCs) for NH$_3$ and diluting gas flows. The experiments were carried out at 26 °C with an accuracy of ± 0.2 °C. The QCM frequency was registered by frequency counter Hameg 8123 connected to the QCM and a computer for data recording. The relative error for frequency measurement was ± 5.25.10$^{-7}$. The sorption ability of the system WO$_3$-QCMs was evaluated on the basis of the measured FTCs. Correlation between the total frequency shift (∆F) and the sorbed mass (∆m) for AT-cut quartz is given by Sauerbrey equation [11], thus the sorbed mass was calculated.

3. Results and discussion

The measured $R_q$ and calculated Q-factor for the samples prepared on different quartz surfaces showed that with the increase of the abrasive grain size the $R_q$ value grows up while the Q-factor decreases. In the investigated interval for 3 μm grain size $R_q = 15.42$ Ω and Q-factor = 27.10$^3$; whereas for 20 μm sample the values reach $R_q = 117$ Ω and Q-factor = 4.10$^3$ respectively. With the increase of the
abrasive size the QCM parameters worsen. Refractive index of 1.94 and thickness of 227 nm were determined for the WO$_3$ films by ellipsometric measurements.

3.1. Sorption properties of WO$_3$-QCM structure

Sorption in one stage was observed for all measured FTCs in the NH$_3$ range of 10 ppm - 50 ppm for QCM realized on surfaces treated with SiC abrasive having grain size of 3 μm and 7 μm. For QCM formed on wafers treated with 14 μm and 20 μm abrasives one stage sorption process was established only at 10 ppm NH$_3$, which is probably due to the lower number of active areas on the rougher surface. Figures 1 and 2 illustrate typical FTCs in the case of one and two stage sorption process, measured at two NH$_3$ concentrations-50 ppm and 500 ppm, when treatment with 3 μm abrasive was conducted. The influence of the initial quartz surface on the sorption properties of WO$_3$-QCM was determined by comparison between FTCs measured at 500 ppm NH$_3$ for all investigated samples. Changes in the frequency shift and frequency recovering for the first 120 s were determined concerning the sorption and desorption processes. The sorption and desorption rates were calculated. The comparison between figure 2 and figure 3 shows decrease in the sorption rate from 0.68 Hz/s to 0.59 Hz/s. The same trend was observed for the desorption process - three times decrease (from 0.45 Hz/s to 0.16 Hz/s) for samples treated with 3 μm and 14 μm. It was found that samples treated with 3 μm and 7 μm give very similar FTC. The one difference is that samples treated with 7 μm possess higher mass-loading ability. The recovery time increases dramatically as compared with samples treated with 14 μm, so such structures are not suitable for sensor application. The results show that the increased roughness embarrasses the sorption process and considerably increases the recovery time of the initial frequency of WO$_3$-QCM structure.

![Figure 1. FTC of WO$_3$-QCM at 50 ppm NH$_3$ - quartz plate treated with 3 μm abrasive.](image1.png)

![Figure 2. FTC of WO$_3$-QCM at 500 ppm NH$_3$ - quartz plate treated with 3 μm abrasive.](image2.png)
The effect of the surface morphology on the maximal frequency shift for WO$_3$-QCM is shown in figure 4. The measurements were carried out in NH$_3$ range of 10 ppm to 1000 ppm. The maximum frequency shift for the samples treated with 14 μm abrasive is higher in comparison with those treated with 7 μm in the whole concentration range. With increasing of NH$_3$ concentration the difference in the frequency shift increases considerably and reaches three times higher values at 1000 ppm. The sorbed mass $\Delta m$ calculated in accordance with the measured frequency shift and the Sauerbrey equation is shown in figure 5. The sorbed mass increases from 15.31 ng for samples treated with 7 μm abrasive to 42.37 ng for those treated with 14 μm at NH$_3$ concentration of 1000 ppm. This means that the rough surface increases the mass loading ability of a WO$_3$ - QCM structure.

The measured sorption properties of the WO$_3$ - QCM structures can be partly explained with results obtained from SEM images for surface morphology and the cross-section profiles of the samples. Figures 6a and 6b illustrate the difference in WO$_3$ layer morphology deposited on the quartz plate and on Au electrode. Comparison between quartz - WO$_3$ and quartz - Au - WO$_3$ systems treated with 7 μm abrasive.
abrasive was made. It is obvious that the roughness of the WO$_3$ layer above Au is considerably higher, because it exactly follows the Au surface. The gradually increase of the WO$_3$ layer roughness of the system quartz - Au - WO$_3$ as a function of the different abrasives is shown in figure 7 a-d. For this purpose all samples were observed at a magnification of $5 \times 10^3$. The surface changes from smooth for the polished samples to clusters. The predominantly grains size when 3 μm abrasive is used was 100 nm, at 7 μm this value increases to 250 nm and reaches size higher than 350 nm for 20 μm abrasive, i.e. the influence of the initial state of the surface is clearly shown.

![Figure 6.](image1.png)

**Figure 6.** Comparison of WO$_3$ surface roughness (7 μm) at magnification 2$x10^4$: a) deposited on quartz plate, b) deposited on Au electrode

![Figure 7.](image2.png)

**Figure 7.** SEM image of WO$_3$ thin film deposited on a) quartz plate - polished - Au; b) quartz plate treated with 3μm abrasive - Au; c) quartz plate treated with 7 μm abrasive - Au; d) quartz plate treated with 20μm abrasive - Au.

![Figure 8.](image3.png)

**Figure 8.** Cross section profiles image of the quartz - Au - WO$_3$ structures: a) polished quartz - Au - WO$_3$; b) quartz (3μm) - Au - WO$_3$; c) quartz (7μm) - Au - WO$_3$; c) quartz (20μm) - Au - WO$_3$.

Deterioration of the equivalent parameters of the investigated WO$_3$ - QCM structures, as well as the difficulties in the sorption and desorption process are largely determined by the way of the Au electrode covering. Figures 8 (a)-(d) show quartz - Au - WO$_3$ profiles of the investigated samples. It can be seen that at the polished surface the WO$_3$ layer is smooth and follows the relief of the Au electrode (figure 8a). At the samples treated with 3 μm abrasive the WO$_3$ layer also follows the relief of the Au electrode, but it was observed presence of pinholes, which are filled. At the treated with 7
μm abrasive samples (figure 8c) the layer is continuous, but with rather rough surface. The quality of coating with 20 μm (figure 8d) is strongly worsened. The continuity of the mass sensitive layer is impaired with hollows. The distortion of the layer continuity causes high acoustic losses and strongly worsens the dynamical parameters of the structures. Discontinuity of the layers is a function of the quartz plate roughness - by its increasing the sorbing surface is enlarged, which results in higher sorbed mass. In the same time the sorption and especially the desorption processes are embarrassed because of the reduced layer’s homogeneity. Depending on the application of the WO$_3$-QCM structures a compromise decision is necessary to be made for saving of the dynamical parameters and increasing of the structures’ sorption ability by increasing of their sorbing surface.

4. Conclusion
In this study the influence of the initial quartz roughness on the WO$_3$-QCM parameters and sorption properties is presented. It is shown that both of them were strongly affected. By increasing the roughness, the mass-loading of the WO$_3$-QCM can be improved. On the base of the obtained results depending on the application a suitable condition for WO$_3$-QCM preparation can be chosen.

Acknowledgements
This work was supported by Bulgarian Ministry of Science and Education under grant NT3/2006 and bilateral project (2009 - 2011) ISSP - BAS and GEOKHI - RAS.

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