Improvement of sensor sensitivity of Quartz Crystal Microbalance by roughening of the piezoquartz plate

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The influence of quartz plate roughening on the dynamic parameters of quartz resonators has been studied. For this aim AT – cut quartz plates with a diameter of 8 mm, having passed a standard technological cleaning, are subjected to treatment with abrasive powders of varying grain sizes - 3, 7, 14 and 20 µm. Piezoquartz resonators are fabricated on these plates with Au electrodes having a diameter of 4 mm. The characteristic parameters of the quartz resonators for the different surfaces at 25^{o}C are as follows:

Resonance frequency, Fs	15,7 MHz ± 100 kHz
Dynamic resistance, Rs	from 15 Ω for quartz plates, treated with SiC grains of 3µm to 120 Ω for quartz plates treated with SiC grains of 20µm
Quality factor, Q	from 28 000 for quartz plates treated with SiC grains of 3µm to 4 000 for plates treated with SiC grains of 20µm

The changes in resonators dynamic parameters after mass loading with a sensitive magnetron sputtered WO_3 layer, 200 nm thick are studied. Quartz Crystal Microbalance sorption properties are evaluated at NH_3 concentration of 100 ppm.
The results show that with increasing of quartz plates' surface roughening the piezoelectric characteristics of the resonators change within admissible limits and the sensor sensitivity is improved.

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1. Introduction

A number of papers deal with the influence of nanometric surface roughening of the quartz plate surface on Quartz Crystal Microbalance (QCM) parameters. A QCM with a quartz crystal coated with roughened tantalum has been used to measure liquids with different concentrations of the active substance [1]. The effect of roughness and surface morphology on QCM response in liquids is studied in [2, 3]. The adsorption of bovin serum albumin on platinum surfaces with roughness ranging from 1, 49 nm to 4,62 nm was investigated using QCM [4]. Angelov et al [5] have studied the sorption sensitivity of AT-cut quartz resonators to moisture using thin fullerene layers for sorbents. It has been shown that a 30% increase of the effective surface results in tenfold increase of sensitivity.

Tungsten oxide (WO_3) has proved to be promising for gas - sensing applications; a number of studies have shown that it can be used for the detection of NOx, CO, ammonia vapours and hydrocarbons [6-9].

This paper reports the results of the method developed for QCM sensitivity increase using the roughening of AT-cut quartz plate surface. The effect of surface roughening on the acoustic parameters of quartz resonators is studied.

The sorption characteristics of QCM with roughened quartz surface coated with WO_3 are studied at 100 ppm NH_3 concentration.

The results obtained indicate that the technology developed can be successfully used in the fabrication of high quality chemical sensors.

2. Experiment

The single crystal quartz used for the fabrication of quartz plates was submitted to cutting in X-sections, cutting of lamberts in plates, orientation, lapping and polishing. AT – cut quartz plates with a diameter of 8 mm were fabricated. For the purpose of this work all plates were processed with a 3 µm abrasive followed by roughening. The figures below show the crystal surfaces measured with an Atomic Force Microscope (AFM). The instrument employed was a Multimode closed loop scanner from Veeco. Imaging was performed in tapping mode and height, amplitude, and phase images were recorded. The scan rate was in range 0.3-0.7 Hz, the images resolution was 256 or 128 (the latter is only for the 20 µm sample) samples/line (lines per scan direction). At least three different points on the sample surface were explored.

Five experimental sets were fabricated. The first one consists of polished quartz plates. It is measured for comparison with the roughened plates (Fig. 1). The next sets comprised quartz plates, processed with SiC abrasive with grain size of 3, 7, 14 and 20 µm. The plates were treated with 3 μm abrasive for achieving such a thickness of the quartz plate that ensures a frequency of 15,7 MHz ± 100 kHz: 120 μm for the 7 μm abrasive, 135 μm – for the 14 μm and 150 μm for the 20 μm.

After standard chemical treatment Au films, 55 nm thick, were thermally evaporated on both sides of the plates through 100 μm thick masks for electrodes.

Resonators were fabricated from these quartz plates. The dynamic capacity Cq, dynamic inductivity Lq and Q – factor were calculated after the measurement of the static capacity C_o, serial resonance frequency F_s and the dynamic resistance R_s. Sensitive WO_3 thin films, 200 nm thick, are deposited by magnetron sputtering on the resonators. The sorption properties of the structures were measured at an ammonia concentration of 100 ppm using laboratory constructed apparatus. The changes in the resonance characteristics of the quartz resonators as a function of the surface roughness were investigated.

3. Results and discussion

3.1. Surface roughness

The results from AFM measurements are presented in Fig. 1- 4.

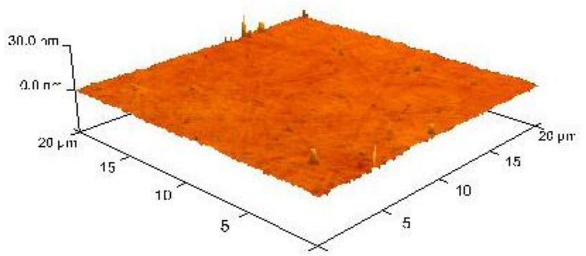

Fig.1. Polished surface. The average roughness is 0.612 nm.

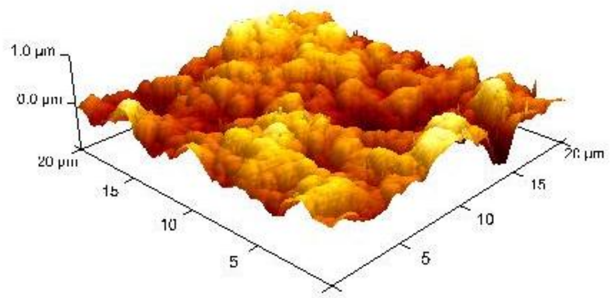

Fig. 2. Surface of a plate processed with 7 μm abrasive. The average roughness is 179 nm.

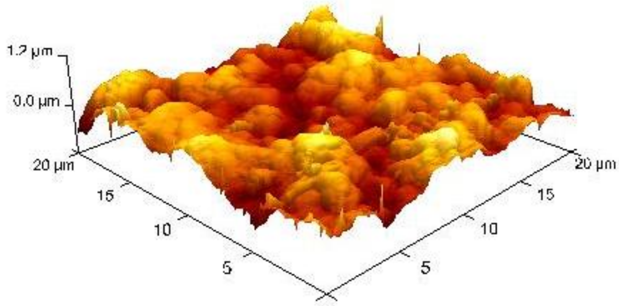

Fig. 3. Surface of a plate processed with 14 μm abrasive. The average roughness is 288 nm.

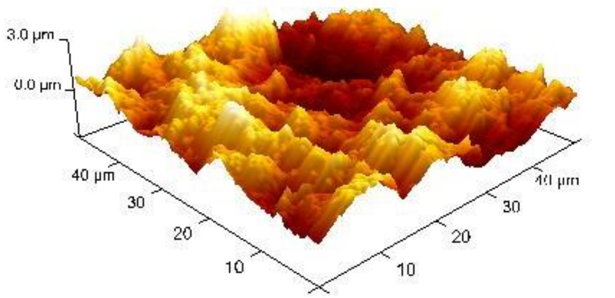

Fig. 4. Surface of a plate processed with 20 μm abrasive. The average roughness is 763 nm.

3.2. Motional parameters

Table 1 presents the averaged measured and calculated dynamic parameters of the experimental sets before and after WO_3 deposition, as well as after the sorption of ammonia vapour.

One can see from Table 1 that the resonators' dynamic parameters deteriorate with increasing surface roughness. This is due to the increased acoustic losses of the resonators. After mass loading of the resonators with WO_3 the dynamic parameters of the polished and roughened with 3 μm plates are deteriorated. Rs_{av} and Q_{av}, improve for surfaces roughened with an abrasive with grain sizes of 7, 14 and 20 μm. That is probably due to a decrease of acoustic losses resulting from the deposition of higher density material (WO_3). One can also see that after the sorption process the dynamic resistance and the Q-factor improve. That could be explained with fact that the dry air of high purity (99.95 %), containing NH_3 in the desired ppm concentrations has a cleaning effect on the surface.

Table 1. Dynamic parameters of experimental samples

Initial parameters of quartz resonators						
SiC grain size (μm)	Fs_{av} (Hz)	Rs_{av} (Ω)	Co_{av} (pF)	Cq_{av} (F)	Lq_{av} (mH)	Q_{av}
Polished plates	15777136	8.67	5.634	2.57×10^{-14}	3.97	45 314
3	15699106	15.42	5.615	2.44×10^{-14}	4.22	27 010
7	15841585	20.78	5.520	2.42×10^{-14}	4.18	19 999
14	15792095	79.10	5.555	2.42×10^{-14}	4.20	5 265
20	15692439	117.00	5.690	2.12×10^{-14}	4.72	4 031
Parameters of Quartz resonators after WO_3 deposition						
Polished plates	15629965	15.23	5.657	2.54×10^{-14}	4.08	26 317
3	15540877	16.10	5.610	2.50×10^{-14}	4.20	25 466
7	15703127	17.60	5.514	2.48×10^{-14}	4.15	23 278
14	15653875	55.80	5.555	2.55×10^{-14}	4.05	7 137
20	15548264	70.30	5.692	2.33×10^{-14}	4.51	6 259
Parameters of Quartz resonators after NH_3 sorption						
Polished plates	15630164	14.10	5.646	2.52×10^{-14}	4.11	28 643
3	15539885	14.84	5.611	2.48×10^{-14}	4.24	27 850
7	15703230	17.06	5.523	2.49×10^{-14}	4.12	23 827
14	15653766	33.80	5.565	2.49×10^{-14}	4.16	12 087
20	15549157	73.65	5.701	2.29×10^{-14}	4.58	6 069

3.3. Sorption characteristics

The sorption sensitivity of WO_3 to NH_3 with 100 ppm concentration is investigated.

The change in QCM resonance frequency as a function of averaged nanometric surface roughness was studied. The results are presented in Table 2. Figure 5 gives the resonance frequency change as a function of abrasive grain size.

Table 2. Frequency change (Δ f) as a function of crystal surface roughening.

SiC grain size (μm)	Roughness (nm)	Δ F (Hz)
Polished plates	0.612	-
3	-	23
7	179	27
14	288	56
20	763	67

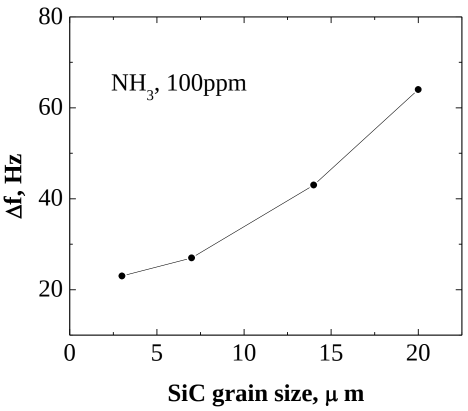

Fig. 5. Change in QCM frequency as a function of abrasive grain size.

Table 2 and Fig. 5 indicate that in spite of the deteriorated dynamic parameters (Table 1) the quartz resonators processed with SiC abrasive with grain sizes of 14 μm and 20 μm and coated with WO_3 have increased sorption sensitivity to NH_3. When the roughness increases about 1250 times the sorption sensitivity increases more 2 times.

4. Conclusion

The dynamic characteristics of quartz resonators with nanometric surface roughness, induced by grinding with SiC abrasive with grain sizes from 3 to 20 μm have been studied. It has been found that the deterioration of the resonance characteristics for resonators processed with an abrasive of 14 and 20 μm grain sizes are due to the increase of resonator acoustic losses.

QCM sorption properties are studied at NH_3 concentration of 100 ppm. The comparison between polished and roughened surfaces indicate that when the nanometric surface roughness increases about 1250 times the sorption sensitivity increases more than 2 times for surfaces processed with 20 μm abrasive grain size.

The results show that with surface roughness increase the piezoelectric characteristics vary within the admissible limits, while the sensor sensitivity increases more than 2 times.

This gives us reason to believe that the roughening of quartz plates can be used successfully to fabricate highly sensitive chemical sensors.

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