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# Improvement of Sensor Sensitivity of Quartz Crystal Microbalance by Mechanical and Chemical Treatment*

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**Abstract.** 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, after a standard technological cleaning, are subjected to treatment with abrasive of varying grain sizes: 3, 7, 14 and 20 $\mu$m. Piezo-quartz resonators are fabricated on these plates with 4 mm Au electrodes. The alterations of resonators' dynamic parameters are followed after mass loading with a sensitive magnetron sputtered $WO_3$ layer, 200 nm thick. Quartz Crystal Microbalance (QCM) sorption properties are evaluated for 100 ppm $NH_3$ concentration; the frequency shift from 20 to 120 Hz, are obtained when the grain sizes change from 3 to 20 $\mu$m. The measured average roughness by Atomic Force Microscopy (AFM) was 179 nm, 288 nm, 763 nm for 7 $\mu$m, 14 $\mu$m and 20 $\mu$m, respectively.

The influence of the etching process of AT-cut quartz plates on the QCM parameters has been studied. Quartz wafers (100 $\mu$m thick, with a diameter of 8 mm), have been etched in $[NH_4]_2$ $F_2$: $H_2O$ = 1:1 solution at temperature range from 70°C to 90°C. The influence of etch treatment on the quartz surface morphology has been estimated by AFM. Sorption properties of QCM-$MoO_3$ are evaluated at $NH_3$ concentrations in the interval from 100 ppm to 500 ppm.

The increase of effective sorption surface, obtained by mechanical and chemical treatment, can be successfully used to realize high sensitive QCM-thin film structure.

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## 1 Introduction

A number of papers deals with the influence of nanometric surface roughening of the quartz plate surface on QCM parameters. Roughness effect on the frequency

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of a quartz-crystal resonator in contact with a liquid has been studied by K. Rechendorff [1]. The adsorption of bovin serum albumin on platinum surfaces with roughness ranging from 1.49 nm to 4.62 nm was investigated using QCM [2]. The influence of the quartz roughness on the QCM-$WO_3$ and QCM-$MoO_3$ dynamic parameters and sorption properties was investigated [3,4].

## 2 Experimental

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 $\mu$m abrasive followed by roughening. The figures below show the crystal surfaces measured with an Atomic Force Microscope (AFM). Five experimental sets were fabricated. The first one consists of polished quartz plates. It is measured for comparison. The next sets comprised quartz plates, processed with SiC abrasive with grain size of 3, 7, 14 and 20 $\mu$m. The plates were processed with 3 $\mu$m abrasive for achieving such a thickness of the quartz plate that ensures a frequency of 15.7 MHz $\pm$ 100 kHz: 120 $\mu$m for the 7 $\mu$m abrasive, 135 $\mu$m-for the 14 $\mu$m and 150 $\mu$m for the 20 $\mu$m. Resonators were fabricated from these quartz plates. Sensitive $WO_3$ thin films, 200 nm thick were deposited by magnetron sputtering on the resonators. The sorption properties of the structures were measured at an ammonia concentration of 100 ppm with a laboratory constructed apparatus.

As results of our experiment the optimal etching time has been defined [4]. The etching system was made of polypropylene. After etching of quartz plates, the samples were subjected to standard chemical treatment. Then Au films, 55 nm thick, were thermally evaporated on both sides. Quartz resonators with basic frequency of 16 MHz $\pm$ 100 kHz were fabricated. From the measured static capacitance Co, serial resonance frequency Fs and dynamic resistance Rs, the dynamic capacity Cq, the dynamic inductance Lq and Q-factor were calculated. The magnetron sputtered $MoO_3$ layers (200 nm) were deposited on the prepared resonators. The sorption properties of the structures were measured at an ammonia concentration of 100 ppm, 250 ppm and 500 ppm with a laboratory constructed set up. The changes in the resonance characteristics of the quartz resonators as a function of the surface roughness were estimated.

## 3 Results and Discussions

The results from AFM measurements of the samples after mecanical treatment are presented in Figures 1 and 2.

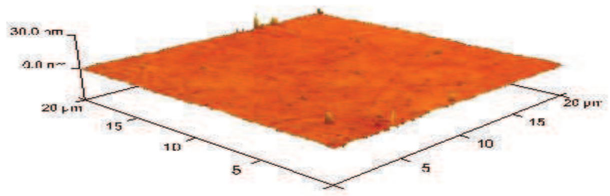


Figure 1: Polished surface. The average roughness (Rq) is 0.612 nm.

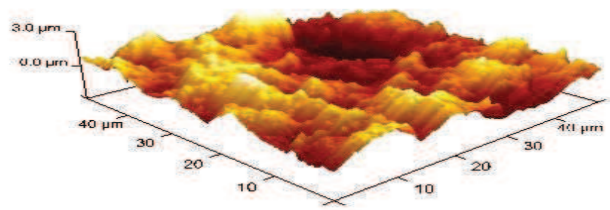


Figure 2: Surface of a plate processed with 20 $\mu$m abrasive. The average roughness is 763 nm.

Table 1: Frequency change ($\Delta F$) as a function of crystal surface roughening

| SiC grain size ($\mu$m) | Roughness (nm) | $\Delta F$ (Hz) |
|---|---|---|
| Polished plates | 0.612 | 21 |
| 3 | — | 23 |
| 7 | 179 | 27 |
| 14 | 288 | 56 |
| 20 | 763 | 67 |

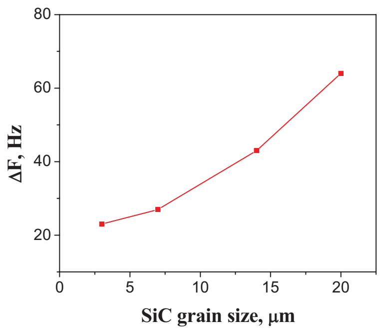


Figure 3: Change in QCM frequency as a function of abrasive grain size.

Table 1 and Figure 3 indicate that when the roughness increases about 1250 times the sorption sensitivity increases more than 3 times while roughness with abrasive with grain size 20 $\mu$m.

The results from AFM measurements of the samples, etched in solution of ammonium bifluoride at different temperatures, are presented in Figures 4 and 5.

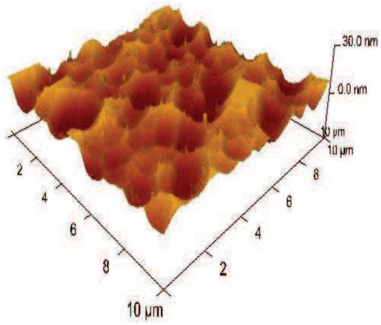


Figure 4: Surface of a quartz plate etched at 70°C. The average roughness is 4.51 nm.

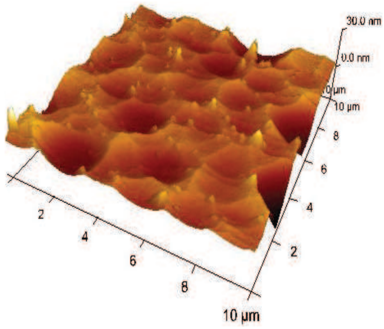


Figure 5: Surface of a quartz plate etched at 85°C. The average roughness is 3.71 nm.

Table 2: Frequency change ($\Delta F$) as a function of etching temperature and average roughness of the quartz surface at different $NH_3$ concentrations

| Etching temperature (°C) | Roughness (nm) | $\Delta F$ (Hz) 100 ppm | $\Delta F$ (Hz) 250 ppm | $\Delta F$ (Hz) 500 ppm |
|---|---|---|---|---|
| 70 | 4.51 | 47 | 205 | 294 |
| 75 | 3.88 | 8 | 23 | 40 |
| 80 | 3.79 | 6 | 20 | 29 |
| 85 | 3.71 | 6 | 18 | 28 |
| 90 | 3.55 | 6 | 16 | 26 |

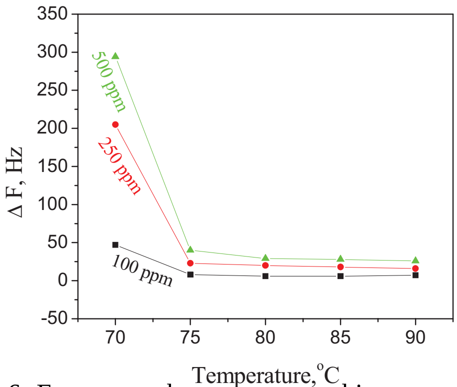


Figure 6: Frequency change versus etching temperature.

It is seen that the difference in the average roughness of plates etched at 70°C and 75°C is 0.63 nm, while the change in sensor sensitivity is 6, 9 and 7.5 times, respectively for $NH_3$ concentrations of 100, 250 and 500 ppm. At etching temperatures of 75°C to 90°C, the roughness increases with 0.33 nm and the sensor sensitivity changes from 1 to 1.5 times respectively.

## 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 $\mu$m have been studied. QCM sorption properties are studied at $NH_3$ concentration of 100 ppm and sensitive $WO_3$ layer, 200 nm thick. The comparison between polished and roughened surfaces indicates that when the nanometric surface roughness increases about 1250 times the sorption sensitivity increases more than 3 times for surfaces processed with an abrasive of 20 $\mu$m 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 3 times.

The dynamic characteristics of quartz resonators obtained etching in $(NH_4)_2F_2$ aqueous solution at temperatures from 70°C to 90°C have been studied. Sorption properties of GAS sensors were tested at $NH_3$ concentration of 100 ppm, 250 ppm and 500 ppm; a $MoO_3$ layer, 200 nm, being used as a sorbent. The difference in the average roughness of plates etched at 70°C and 75°C is 0.63 nm, while the change in sensor sensitivity is 6, 9 and 7.5 times, respectively for $NH_3$ concentrations of 100, 250 and 500 ppm. At etching temperatures from 75°C to 90°C the effective sorption surface is reduced due to the reaction mechanism. It has been found that the samples etched at 70°C have the best sorption sensitivity.

The increase in effective sorption surface, obtained by mechanical and chemical treatment, can be used successfully to fabricate highly sensitive gas sensors.

## References

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