Improving Resonance Characteristics of Gas Sensors by Chemical Etching of Quartz Plates

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Abstract. The paper presents the results of the influence of the etching process of AT-cut quartz plates on the resonance parameters and the QCM sensors. Quartz wafers (100 µm thick, with a diameter of 8 mm), divided into five groups, have been etched in [NH₄]₂F₂: H₂O = 1:1 solution at temperatures in the range from 70°C to 90°C. The influence of etching temperature on the surface morphology of quartz wafers has been estimated by Atomic Force Microscopy (AFM). A correlation between the etching temperature and the dynamic characteristics is obtained. The optimal etching conditions for removing the surface damages caused by the mechanical treatment of the quartz wafers and for obtaining a clean surface were determined. The typical parameters of fabricated resonators on the quartz plates etched in the temperature range from 70°C to 90°C are as follows:
- Frequency, Fs: 16 MHz ± 100 kHz
- Motional resistance, Rs: less than 10 Ω
- Motional inductance, Lq: higher than 3 mH
- Motional capacitance, Cq: less than 30 fF
- Static capacitance, Co: around 5 pF
- Quality factor, Q: from 46 000 to 70 000

Sorption properties of QCM - MoO₃ are evaluated at NH₃ concentrations in the interval from 100 ppm to 500 ppm.

1. Introduction
The surface state of a quartz plate is responsible for the resonators’ quality. Its change leads to alteration of the resonators’ parameters. Roughness effect on the frequency of a quartz-crystal resonator in contact with liquid is studied by K. Rechendorff [1]. The influence of nanometre scale surface roughness on the frequency of a quartz crystal microbalance operating in a liquid environment has been investigated by exposing quartz crystals, with a rough tantalum coating, to water solutions with varying concentrations of sucrose. A clear correlation between the measured surface roughness and the frequency shift is observed.

The different roughness of the quartz surfaces can be achieved by treatment with abrasive with different grain size or by chemical etching. The influence of the quartz roughness on the WO₃-QCM parameters and sorption properties was investigated [2]. Experiments were carried out using AT-cut
quartz crystal with surface roughness obtained by treatment with SiC abrasive with grain size from 3 μm to 20 μm. The correlation of the equivalent dynamic parameters of the structure and the surface roughness was determined. The surface morphology showed higher increase of the WO₃ surface roughness compared to the initial quartz surface. The sorption properties of WO₃-QCM system to NH₃ showed an increase of the sorption ability with the increase of the quartz roughness.

The authors in [3] investigated the lapping and polishing processes of quartz in relation to crystalline orientation. The measurements of the surface roughness were carried out in X-, Y-, Z- and AT-cut samples. It shows that the relationship found between material removal rate and stress depends on specimen orientation. Surface profiles and SEM micrographs show that roughness of lapped surfaces decreases with increasing the normal stress but an opposite behaviour is observed in polished surfaces. It is well known, that when the AT-cut lapped quartz is etched in saturated solution of ammonium bifluoride [NH₄]F, the surface roughness decreases. This way with increasing the depth of the etching, the plates became chemically polished. The same effect takes place for single rotated BT-cut and ST-cut, but not for double rotated IT and SC-cuts. With increasing the depth by the etching in [NH₄]F₂ solution, the surfaces of quartz plate become rougher as a result of the etching process.

Fundamental studies of chemical etching of quartz were carried out by Watanable [4, 5].

The etch rate and surface roughness of polished and lapped AT-cut quartz subjected to hot (90, 110, and 130°C), concentrated (50, 65, 80 wt %) [NH₄]F₂ have been investigated. Etch rates were found to correlate well, and possibly logarithmically, with temperature except for the hottest etching applied to lapped material. Roughness as a function of temperature and concentration behaved well for the lapped material, but lacked systematic variation in the case of the polished material. At the lowest temperature, concentration had no effect on the etch rate or roughness. Their future efforts are targeted at temperatures and concentrations closer to the solubility limit [6].

The aim of the work is to study the influence of etching process of AT-cut quartz in [NH₄]F₂ solution at low temperature (70°C-90°C) on quartz roughness, on resonator parameters and sorption sensibility of the QCM-MoO₃ structure.

2. Experimental
Quartz wafers (100 μm thick, with a diameter of 8 mm), divided into five groups, have been etched in [NH₄]F₂:H₂O = 1:1 solution at temperatures in the range from 70°C to 90°C.

The etching system was made of polypropylene. The etching bath was put in a thermostat, the temperature being stabilized in a water bath. The temperatures of the water and the etchant were controlled by a digital thermometer (Delta Instruments with accuracy of ±0.2°C) placed in a polypropylene tube. The typical temperature difference between the etchant and the water bath was 2°C. The plates were put vertically in a polypropylene holder, which was shaken occasionally in order to homogenize the etchant. Optimal time for etching is determined by the results, obtained in treatment of three series at temperatures 75°C, 80°C and 85°C that show the change of frequency as the result of etching duration.

Figures 2-4 show the crystal surfaces of the quartz plates measured with an Atomic Force Microscope (AFM). AFM measurements were carried out using a Multimode V (Veeco, Santa Barbara, CA) equipped with closed loop scanner. Imaging was performed in tapping mode and height, amplitude, and phase images were recorded. Scan rate was in range 1.0-1.5 Hz, the images resolution was 512 samples/line. At least three different points on the sample surface were explored. Silicon cantilevers with a cantilever length of 125 μm and Al Reflective coating on the backside (RTESPA, Veecoprobes) were used in the experiments. RTESPA probes have a nominal resonance frequency of 300 kHz and a typical force constant of 40 N/m. The tip nominal radius for these probes is less than 10 nm. Image processing was performed by means of Nanoscope 7.30.

After etching of quartz plates, the samples were subjected to chemical treatment that consists of samples boiling for 30 min in H₂SO₄ : H₂O₂ = 1 : 3 and than followed rinsing in deionised water. Then Au electrodes (55 nm thick) with diameter of 4 mm were thermally evaporated on both sides of the plates. As a result of the above technological procedures, quartz resonators with basic frequency of 16 MHz ± 100 kHz were produced. After measuring the static capacitance Co, the serial resonance frequency Fs and dynamic resistance Rs, the dynamic capacity Cq, the dynamic inductance Lq and Q-factor were calculated. The average values of the equivalent dynamic parameters are marked with-(av)
index.

Thin MoO$_3$ layers 200 nm were deposited by magnetron sputtering on both sides of the resonators. The sorption properties of the QCM-MoO$_3$ structures were measured at ammonia concentration of 100 ppm, 250 ppm and 500 ppm on a laboratory set up. The changes in the resonance characteristics of the quartz resonators, as a function of the surface roughness, were measured.

3. Results and discussion
The quartz plate frequency change versus etching time at different temperatures is shown on figure 1.

![Figure 1. Frequency dependence versus etching time.](image1)

Figure 1 demonstrates the greatest change of the frequency which reaches up to 60 s. The high etching rate of 60s is caused by the great number of free chemical bonds on the quartz surface, resulting from the mechanical treatment. Negligible dependence changes are observed at etching time from 120s to 180s. The optimal time for etching - 120s was obtained. It shows that the frequency change occurs after the 120$^{th}$ second. The influence of the etching time and temperature of quartz surface relief and morphology was studied by Atomic Force Microscopy (AFM).

3.1. Surface roughness
The results from AFM measurements of the samples, etched in solution of ammonium bifluoride at different temperatures, are presented in figure 2-4.

![Figure 2. Quartz surface etched at 70°C. The root mean square roughness is 4.51 nm.](image2)
3.2. Motional parameters

Table 1. Dynamic parameters of experimental samples

| Etching temperature, °C | $F_{\text{av}}$, Hz | $R_{\text{av}}$, Ω | $C_{\text{av}}$, pF | $C_{\text{q}, \text{av}}$, F | $L_{\text{q}, \text{av}}$, mH | $Q_{\text{av}}$ |
|-------------------------|---------------------|-------------------|-------------------|----------------|----------------|-------------|
| 25                      | 1577136             | 8.67              | 5.634             | 2.57E-14        | 3.97           | 45 314      |
| 70                      | 16105181            | 5.80              | 5.700             | 2.73E-14        | 3.57           | 62 341      |
| 75                      | 16084578            | 5.20              | 5.715             | 2.72E-14        | 3.16           | 70 079      |
| 80                      | 16118224            | 6.03              | 5.610             | 2.69E-14        | 3.63           | 60 862      |
| 85                      | 16196423            | 7.41              | 5.720             | 2.84E-14        | 3.41           | 46 800      |
| 90                      | 16509816            | 7.68              | 5.690             | 2.70E-14        | 3.45           | 46 537      |

Quartz resonators parameters after MoO$_3$ deposition

| Etching temperature, °C | $F_{\text{av}}$, Hz | $R_{\text{av}}$, Ω | $C_{\text{av}}$, pF | $C_{\text{q}, \text{av}}$, F | $L_{\text{q}, \text{av}}$, mH | $Q_{\text{av}}$ |
|-------------------------|---------------------|-------------------|-------------------|----------------|----------------|-------------|
| 25                      | 15629965            | 15.23             | 5.657             | 2.54E-14        | 4.08           | 26 317      |
| 70                      | 16010547            | 6.70              | 5.700             | 2.69E-14        | 3.68           | 55 163      |
| 75                      | 15994868            | 5.66              | 5.724             | 2.59E-14        | 3.82           | 67 827      |
| 80                      | 16029757            | 9.15              | 5.605             | 2.43E-14        | 4.06           | 44 662      |
| 85                      | 16106289            | 9.00              | 5.727             | 2.42E-14        | 4.04           | 45 372      |
| 90                      | 16416009            | 8.90              | 5.694             | 2.42E-14        | 3.89           | 45 088      |

Quartz resonators parameters after NH$_3$ sorption

| Etching temperature, °C | $F_{\text{av}}$, Hz | $R_{\text{av}}$, Ω | $C_{\text{av}}$, pF | $C_{\text{q}, \text{av}}$, F | $L_{\text{q}, \text{av}}$, mH | $Q_{\text{av}}$ |
|-------------------------|---------------------|-------------------|-------------------|----------------|----------------|-------------|
| 25                      | 15630164            | 14.10             | 5.646             | 2.52E-14        | 4.11           | 28 643      |
| 70                      | 15995672            | 6.65              | 5.738             | 2.69 E-14       | 3.69           | 55 740      |
| 75                      | 15995359            | 5.60              | 5.719             | 2.57 E-14       | 3.35           | 69 058      |
| 80                      | 16030250            | 8.95              | 5.597             | 2.43 E-14       | 4.06           | 45 712      |
| 85                      | 16107048            | 6.28              | 5.565             | 2.44 E-14       | 4.01           | 64 546      |
| 90                      | 16416522            | 8.51              | 5.694             | 2.43 E-14       | 3.36           | 46 822      |
Table 1 shows that the quartz resonators created at room temperature (25°C) have less favorable resonance characteristics (Rs, and Qs are respectively 8.67 Ω and 45 314) compared to the ones with temperature treatment, which leads to the necessity of thermal treatment of the quartz plates. After mass loading of resonators with MoO₃, their dynamic parameters get worse. For example: when etching quartz plates at temperature of 70°C, Rs of the resonators gets from 5.80 Ω to 6.70 Ω and Qs gets from 62 341 to 55 163. When etching temperature is 90°C, Rs of the quartz resonators gets from 68 Ω to 8.90 and Qs from 46 537 to 45 088.

Resonators’ dynamic parameters deteriorate after mass loading with MoO₃. This is presented in table 1. It could be explained by the resonators’ increased acoustic losses.

After sorption, the values of the dynamic resistance and Q get better. For example: when etching quartz plates at temperature of 70°C, Rs of the resonators gets from 6.70 Ω to 6.65 Ω, and Qs changes from 55 163 to 55 740. When etching quartz plates at temperature of 90°C, Rs of the resonators gets from 8.90 Ω to 8.51 Ω, and Qs gets from 45 088 to 46 822. The reason for this is the excellent cleaning of quartz surface after it has been treated with dry air with high frequency (99.95%), which also contains a certain NH₃ concentration.

3.3. Sorption characteristic.
The change in QCM-MoO₃ resonance frequency as a function of quartz surface roughness is studied. The sorption sensitivity to NH₃ with concentration of 100 ppm, 250 ppm and 500 ppm is investigated. The results are presented in table 2 and in figure 5.

| Etching temperature, °C | Roughness, nm | f, Hz at 100 ppm NH₃ | f, Hz at 250 ppm NH₃ | f, Hz at 500 ppm NH₃ |
|-------------------------|--------------|----------------------|----------------------|----------------------|
| 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                   |

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 7.4 times, respectively for NH₃ concentrations of 100, 250 and 500 ppm. At etching temperatures of 75°C to 90°C, the roughness decreases with 0.33 nm and the sensor sensitivity changes from 1 to 1.5 times for all concentrations respectively. As a result of the mechanical treatment, a stress increases in the crystal could lead to micro cracks. Also, as a result of this treatment, a lot of free chemical bonds are retained, which can absorb moisture and gases from the environment. The aim of the etching is removing this disturbed surface layer. On the quartz surface reside silicon atoms that form single, double and triple bonds to the crystal lattice. In water soluble systems, the oxygen atoms on the quartz surface combine with protons and form hydroxyl groups. Water solutions of (NH₄)₂F₂ contain F and HF₂⁻ ions. The F⁻ ions can replace the OH-groups. The process of substitution for double bonded to the lattice surface atoms involves a further sorption of HF₂⁻ ions. This step in the reaction mechanism leads to releasing SiF₄, which has good solubility in the etchant by the following reaction:

\[
\text{SiO}_2 + (\text{NH}_4)_2\text{F}_2 \rightarrow \text{SiF}_4 + \text{NH}_3\text{OH}
\]

The quartz surface relief became smoother as results of this mechanism.
The effective surface area is the highest at etching temperature of 70°C. This leads to a greater sorption of NH₃.

4. Conclusion.
The etching process of AT-cut quartz in (NH₄)₂F₂ aqueous solution at low temperature from 70°C to 90°C was studied. The created resonators on so treated quartz plates retain their equivalent dynamic parameters. The AFM analysis on quartz roughness shows that the greatest quartz roughness is obtained at 70°C. At etching temperatures from 75°C to 90°C the effective surface is reduced due to the reaction mechanism. It was shown that the difference in the average roughness of quartz plates etched at 70°C and 75°C of 0.63 nm, leads to sensitivity increase of QCM-MoO₃ in 6, 9 and 7.5 times, for NH₃ concentrations of 100, 250 and 500 ppm respectively.

The increase of effective sorption surface, obtained by chemical etching, can be successfully used to realize high sensitive gas sensors.

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