Influence of nano-objects positioning on sensitivity of QCM sensor

P O Novichkova\textsuperscript{1}, A R Vechkanov\textsuperscript{1}, S V Yanovitch\textsuperscript{2}

\textsuperscript{1}RUDN University (Peoples’ Friendship University of Russia), 6 Miklukho-Maklay St., Moscow, 117198, Russia
\textsuperscript{2}Bauman Moscow State Technical University, 2nd Baumanskaya street, 5, Moscow, Russia

E-mail: yanovich.sv@gmail.com

Abstract. Dependence of the sensitivity of the QCM sensor on the position of the object relative to the centre of the sensor is considered. Comparison of calculating mass increment and measured values in cases of various fillings and displacement of nanoobjects was carried out.

1. Introduction

QCM (Quartz Crystal Microbalance) or the piezoelectric micro-weighing method is a mass measurement tool which is based on the dependence of the oscillation frequency of the quartz sensor on the amount of matter deposited on its surface. When calculating the mass increment in general case it is assumed that the entire mass is evenly distributed over the sensor electrode, during biological and chemical studies the mass may occupy a smaller area on the sensor electrode or be displaced relative to the center. In such cases the sensitivity of the sensor changes.

To estimate the occurring imprecision it is proposed to create on the surface of the QCM sensor a silver film with a thickness of up to 100 nm of different area and with different distance from the center of the sensor using PVD method. Using PVD method will produce films of the same thickness and density. Assessment of change of sensitivity of the quartz sensor at different locations of the mass increment will allow to estimate imprecision at the stage of laying of the test substance to the sensor and increase sensitivity of measurement.

2. Theoretical part

When calculating the increments of micromass thin-film objects on the surface of a piezoquartz sensor, the Sauerbrey equation [2] is used:
\[ \Delta f = - \frac{2 f_0^2}{S \sqrt{\rho_q \mu_q}} \Delta m_n \]  

(1)

where \( \Delta f \) is the change in the oscillation frequency of the resonator caused by the application of a film coating, Hz; \( f_0 \) is the natural resonant frequency of quartz oscillations, Hz; \( S \) is the film area, mm\(^2\); \( \rho_q \) is the density of quartz \( 2.648 \text{ g/cm}^3 \); \( \mu_q \) is the shear modulus for quartz AT-cut crystal \( 2.947 \times 10^{11} \text{ g·cm}^{-1}·\text{s}^{-2} \); \( \Delta m_n \) is the mass of the silver film coating, ng.

The calculation of the increment of the mass of the silver film coating [3]:

\[ \Delta m_n = - \frac{4.419 \times 10^5 \Delta f \cdot S}{f_0^2} \]  

(2)

Formula (2) is calculated for the case of complete and uniform filling of the surface of the working electrode of the sensor with a substance. For the case of non-uniform filling, it is proposed to introduce coefficients that are determined experimentally. The options for complete filling (a), partial filling (b) and shifting (c) are shown in Figure 1.

Fig. 1. Variants of the location of the mass increment on the working electrode of the sensor

The sensors have a different topology, in accordance with which the values of displacements and diameters are chosen. The ranges of mass values for varying the area of the coating from 2 to 12 mm. Rate shear coverage from 0 to 5 mm.

3. Experimental part

PVD unit

Silver films were formed by evaporation in a vacuum onto quartz sensors through a mask. For this purpose, a vacuum unit with oil-free pumping of UVN 71-T1 was used.

Extreme pressure – 2.0 \( \times 10^{-4} \) Pa, Working pressure - 1.5 \( \times 10^{-3} \) Pa, Application speed - 5 nm/min, Distance to the substrate – 150 mm.

Sensor

Mass sensor is based on the 10 MHz AT-cut crystal element. The crystal element is with diameter of 14.5 mm. The surface treatment is polishing. Electrodes are made with a diameter of 12 mm (working) and 8 mm. The electrode material is silver

Measuring stand

The measuring bench is assembled on the basis of the measuring unit CPNA-330 (NPF CJSC ETNA) which is based on a vector network analyzer in the frequency range from 1 KHz to 330 MHz. The stand allows you to measure by the method of QCM-I.

![Connection diagram of the mass sensor](image)

Fig. 2 - Connection diagram of the mass sensor

The mass sensor (MS) is installed in the measuring cell (MC), which is connected to the reflectometer (Ref.) And the vector analyzer (CPNA-330). Measurement processing is done using PC software.

Experiment

Experiments were carried out to form discrete elastic coatings with a thickness of up to 100 nm by thermal spraying of silver onto the quartz sensors, from which the dependence of sensitivity on the fill
factor and displacement was obtained. The silver coatings were applied to the quartz sensors through masks, the topology of which provides for different deviations and fillings of the sensor.

To assess the influence of the coating area, the thin-film coatings of the same thickness (up to 100 nm) were applied, in the form of circles with diameters of 2, 5, 8, and 12 mm. The mass of these coatings is shown in Figure 3.

Fig. 3 - Graph of the increment of mass of the coating area, where:
\( \Delta m \) is the mass increment in the cassettes 1 and 2, \( m \) is the theoretical mass increment for a given area.

To assess the effect of shear with the same area of the coating, thin film coatings were applied with the same thickness (up to 100 nm), in the form of circles with the diameter of 2 mm and shifts from the center: 0; 1.5; 3.5; 5 mm. The mass of these coatings is shown in Figure 4.
4. Discussion of the results

The sensors investigated have anisotropy of properties in the working plane. When the mass is shifted along different crystallographic axes the mass increment will be different. If the film is formed uniformly and its center coincides with the center of the electrode the imprecision associated with the anisotropy is compensated and does not affect the measurement results.

In case of full filling of the electrode with the uniform homogeneous coating the measured value is close to the calculated value. As the coverage area decreases the measurement imprecision increases. In the area that corresponds to the lower electrode (diameter 5 mm) with further reduction an error can reach 25% (for an area of up to 2 mm).

The original samples (without displacement) are equal in mass but at displacement mass values begin uneven decline. The orientation of the displacement direction relative to the crystallographic axes in the plane of the sensor was not carried out, at that owing to the anisotropy of piezocrystals quartz, the difference of the measured mass can reach 30% of the estimated value when displacing in a random direction. With a 1.5 mm displacement this spread is 150 ng.

In general such imprecisions occur due to uneven distribution of volume acoustic waves, the amplitude of which has its maximum in the center of the sensor and attenuates as the distance to the edge.

Changing of area and location of nanostructures implies their uniform distribution in the volume. If the samples are not uniform the measurement imprecisions will increase further according to the distribution and displacement of the mass increment.

5. Conclusion

Measurement of discrete coatings that occupy less than 20% of the working electrode area increases the measurement imprecision. Displacement in a random direction introduces an imprecision...
due to an additional component caused by the anisotropy of the properties of the piezocrystalline sensor and damped volume acoustic waves.

When carrying out measurements using QCM in which the area of nano-objects is less than the area of the electrode or they are located with an offset it is necessary to take into account the imprecisions associated with the electrophysical properties of the sensor and the mass distribution in the volume of the sample.

References
[1] Alder J. F. 1983 Analyst 1291 1169.
[2] Sauerbrey G Z 1959 Z. Phys. - B. 155 206.
[3] Malov V V 1989 M.: Energoatomizdat., 272. - ISBN 5-283-01507-6.