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Out-of-plane vibrations of quartz resonators used in quartz crystal microbalance measurements in gas phase

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Abstract

The article reveals that shear-mode quartz crystal resonators, currently used in quartz crystal microbalance (QCM) measurements, exhibit an out-of-plane vibration without being in contact with a liquid. Laser assisted CVD was used to deposit carbon-nanoparticles on the surface of a quartz resonator. The in-plane, shear vibration of the quartz resonator, produces a mega-gravity acceleration which induces a sedimentation of the carbon-nanoparticles, while the out-of-plane vibration produces a mega-gravity acceleration, normal to the crystal surface, which induces an expelling of the deposited carbon-nanoparticles. The two opposite effects reveal a complex situation on the quartz resonator surface in QCM measurements.

Keywords: Quartz; Vibration; QCM; Acceleration; Mega-gravity

1. Introduction

Ever since quartz crystal resonators have been used for frequency control in radio-communication equipment, the effect of a foreign material deposited on their surfaces on the resonant frequency has been known. However, a quantitative relationship was not established until 1959. The possibility of using quartz crystal resonators as quantitative mass measuring devices was first explored by Sauerbrey [1]. The decrease of the resonant frequency of a thickness shear vibrating quartz crystal resonator, having AT or BT cut was found to be proportional to the added mass of the deposited film:

$$\Delta f = -\frac{f_q^2 M_f}{N\rho_q S} = -\frac{f_q^2 m_f}{N\rho_q} \quad (1)$$

where f_q is the fundamental resonant frequency of the quartz, N the frequency constant of the specific cut ($N_{AT} = 1.67 \times 10^5$ Hz cm; $N_{BT} = 2.5 \times 10^5$ Hz cm), $\rho_q = 2.65$ g/cm^3 is the quartz density and S is the surface area of the deposited film, the mass of which is M_f. When the deposited film covers the whole sensitive area of the quartz resonator it is easier to use the areal density $m_f = M_f/S$ to further calculate the thickness $l_f = m_f/\rho_f$, where ρ_f is the density of the deposited film. A typical quartz crystal resonator is shown in Fig. 1. The key-hole shaped electrodes on both major faces of the quartz resonator are vacuum deposited gold or silver films, about 150 nm in thickness. The mass sensitive area is situated in the central part of the resonator, covering about the area where the two electrodes overlap.

QCM became a largely used instrument for small mass measurements in vacuum and gas phase [2,3] and, from 1980, in liquid phase [4].

The in-plane shear vibration of a quartz resonator having AT-cut, usually used in QCM measurements, generates shear waves in contacting liquid, which are strongly damped by the viscous liquid. Thus, only a thin layer of liquid is entrained in a shear motion, leading both to a frequency change and to a decrease in the quality factor of the quartz resonator.

The frequency change, when one face of an AT-cut quartz resonator is in contact with a liquid was first calculated by Kanazawa and Gordon [5] and later using the energy transfer

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model [6]:

$$\Delta f = -f_0^{3/2}\sqrt{\frac{\rho_l \eta_l}{\pi \rho_q \mu_q}} \quad (2)$$

where f_0 is the quartz resonator frequency vibrating in its fundamental mode, ρ_q and μ_q the quartz density and shear modulus, while ρ_l and η_l are the liquid density and viscosity.

During QCM measurements in liquids became evident that some compressional waves are also generated in the liquid and these waves, being less attenuated in the liquid, are travelling on a long distance and reflected by the liquid–air interface or some surfaces parallel to the crystal surface. The origin of these compressional waves was explained by Martin and Hager [7]. They revealed that the velocity gradients in the entrained liquid displacement are responsible for the generation of the compressional waves in liquids. Reddy et al. [8] considerred also the possibility that flexural vibrations are coupled to the shear vibrations. Thus, compressional waves in liquids originates both from velocity gradients in contacting liquid and from flexural vibrations of the crystal itself. EerNisse et al. [9] revealed, using FEA, that AT-cut resonators exhibit a flexural motion associated to their shear motion. This out-of-plane motion can contribute to the compressional waves in the contacting liquid. Portnoff et al. [10] used the resonant energy absorption when standing-waves are produced in the gap between the surface of an AT-cut quartz crystal resonator and a parallel reflecting wall. The results obtained with a plano-convex 5 MHz quartz crystal resonator and a parallel reflecting wall with a diameter of 2 mm are shown in Fig. 2. At different locations along the *X*-axis of the quartz resonator the gap length was increased slowly to pass the condition for standing-waves:

$$d = n\frac{\lambda}{2} = 0.03164\,\text{mm}$$

The frequency of the AT-cut quartz crystal resonator was 5.029 MHz and the wavelength in air was $\lambda = 0.0633$ mm. An increase in the quartz resonator series resistance was detected on two locations along the *X*-axis, symmetrically situated with respect to the crystal centre, for both $n = 1$ and 2. The two peaks have not the same height, probably because of a slight deviation from the *X*-axis. More details are presented in [10].

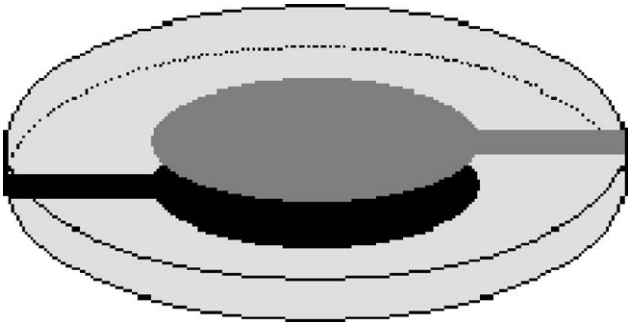

Fig. 1. A typical quartz crystal resonator.

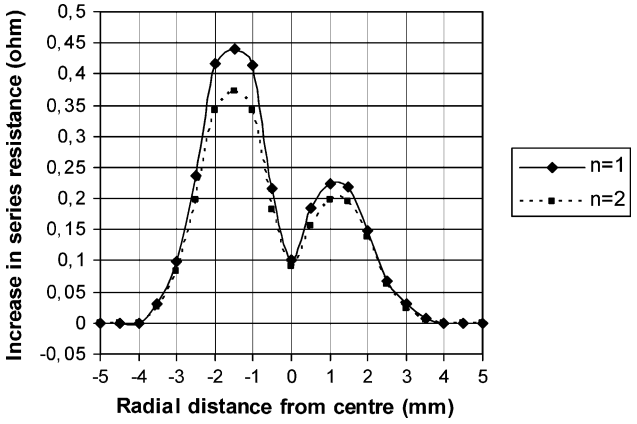

Fig. 2. Experimental evidence of the out-of-plane compressional waves along the *X*-axis of a 5 MHz plano-convex AT-cut quartz crystal resonator using standing-waves in air.

The aim of the present article is to provide an additional experimental evidence of the fact that a quartz resonator, vibrating in a shear mode, generates out-of-plane vibrations on its surface, without being in contact with a liquid.

2. Experimental

The experiments were performed using QCM-3 equipment and CSPO-1 power oscillator, which permits a high drive level of the quartz resonators up to 150 mA. Using automatic level control (ALC) the crystal current could be scanned between 1 and 100 mA with different rates.

A 6 MHz AT-cut plano-convex quartz resonators (Maxtek P/N 103200 and P/N 103218), with gold electrodes and a diameter of 14 mm were used in the experiments.

The carbon covered iron-nanoparticles were deposited by a laser assisted chemical vapor deposition (L-CVD) system consisting of a vaporizing/sublimation chamber and a deposition chamber. An ArF excimer laser was used, operating at a wavelength of 193 nm, 50 Hz (nominal pulse duration: 15 ns [FWHM]) and a fluence of around 110 mJ/cm^2. The plane of the laser beam was parallel to the crystal surface. It was focused with a cylindrical lens achieving a focusing area above the QCM crystal of 0.13 cm^2 located at around 2 mm above the crystal.

The precursor, ferrocene, was vaporized/sublimated at a temperature of 43 °C and introduced into the deposition chamber by the carrier gas Ar. The gas mixture of ferrocene and argon travelled parallel with the laser beam for 10 cm before reaching the deposition zone. Total pressure in the system was 30 mbar with a linear gas velocity of 8 cm/s along the laser beam. The deposition time was 40 min. The carbon-nanoparticles were produced in the laser beam above the quartz resonator. They reached the surface of the quartz resonator not only by gravity, but also by the mega-gravity inertial field developed during crystal vibration [11].

3. Results

In Fig. 3, a quartz resonator coated with carbon-nanoparticles for 40 min, while the crystal current was 90 mA is shown.

Although the laser beam was about 20 mm wide and the crystal was placed about 3 mm under the laser beam, the deposition was located only in the central part of the resonator where its vibration is located. This might be interpreted as a sedimentation induced by the mega-gravity field of the shear vibrations in the centre of the crystal. The deposition also reveals some lines radiating from the centre with significant difference in thickness. Those locations where the carbon film is thinner are regions where the crystal vibration has an out-of-plane component. At these locations the acceleration of the vibrations normal to the crystal surface is high enough to expel the carbon-nanoparticles, which accumulates at the nodal locations. This experimental result is in accordance with the calculations made by EerNisse et al. [9] for flexural vibrations associated to the normal shear vibrations of the AT-cut resonators. The fact that deposition is located mostly in the central part of the resonator might be interpreted as a proof that shear vibrations induce a sedimentation of the deposited carbon-nanoparticles. It is a competition between sedimentation induced by shear vibrations and expelling induced by out-of-plane vibrations of the crystal. The deposition has an elliptic form, probably because the carbon-nanoparticles were "blown" by the gas stream parallel with the laser beam and the plane of the quartz crystal resonator. The elongated area without carbon-nanoparticles is the area where an out-of-plane vibration is present on the crystal surface. The two regions where out-of-plane compressional waves are generated are not clearly revealed in this picture as expected from the results shown in Fig. 2. By increasing the crystal current this effect becomes evident. In Fig. 4, a resonator coated with carbon-nanoparticles, while the crystal was placed 1 mm under the laser beam and the crystal current was 140 mA is shown. It reveals two lobes, symmetrically positioned versus crystal centre. These lobes correspond to the two peaks shown in Fig. 2. The carbon-nanoparticles were also expelled because of the high acceleration. The amplitude of the out-of-plane vibrations in these regions is about 6% of the maximum amplitude of the shear vibration in the centre of the crystal [9]. Today it is not possible to calculate the exact magnitude of the shear vibration in the centre of a plano-convex 6 MHz quartz crystal resonatot. However, Borovsky et al. [12] provided an equation for the calculation of the magnitude of the shear vibration in the centre of a plano-plano 5 MHz quartz crystal resonator. Thus, the amplitude of the shear vibration of a plano-convex, 6 MHz quartz crystal resonator can only be estimated using the equation established by Borovsky et al. [12], the recently formulated and demonstrated acceleration dependent mass sensitivity principle [11] and a comparison of the mass sensitivities in the centre of a 5 MHz plano-plano crystal and a 5 MHz plano-convex crystal [13]. In our case it is about 100 millions times higher than the gravitational acceleration. Thus, the acceleration of the out-of-plane vibrations in the region of the two lobes is about 6 million times higher than the gravitational acceleration. This acceleration develops a force, normal to the crystal surface, that exceeds the binding force of the carbon-nanoparticles agglomerates to the gold electrodes. In Fig. 5, a SEM picture of an area located at the edge of one of the two lobes is shown. This reveals the expelling of the carbon-nanoparticles agglomerates in the region with a high acceleration normal to the crystal surface. The average diameter of the carbon-nanoparticle agglomerates is about 3 μm. It is possible that these expelled

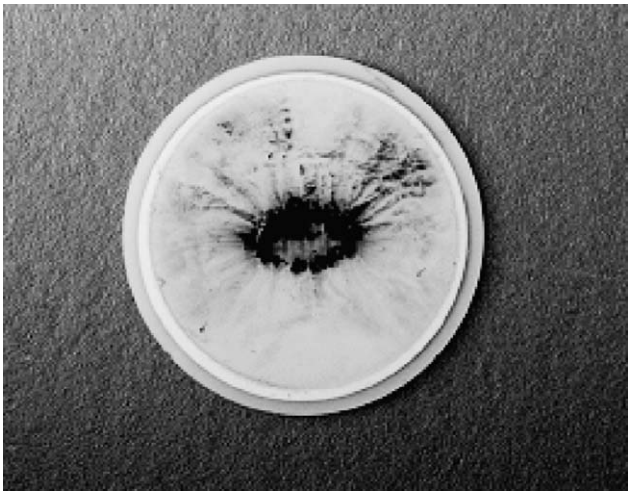

Fig. 3. A 6 MHz plano-convex AT-cut quartz resonator coated with carbon-nanoparticles for 40 min, while the crystal current was 90 mA.

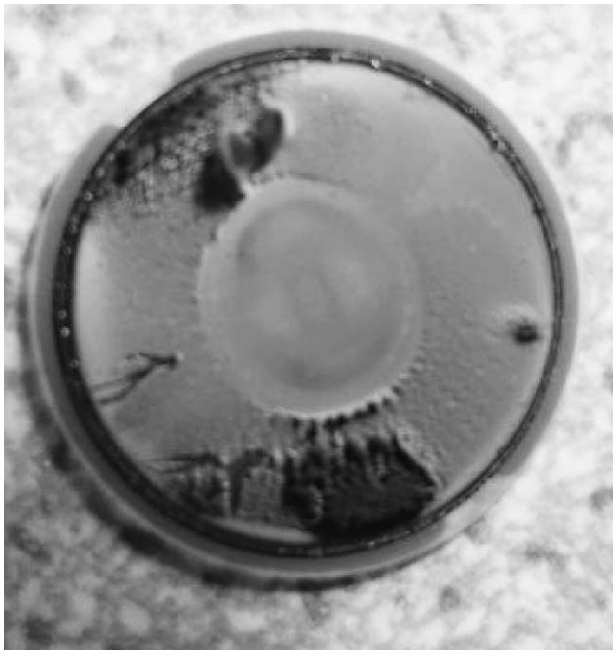

Fig. 4. A 6 MHz plano-convex, AT-cut quartz resonator coated with carbon-nanoparticles while the crystal current was 140 mA.

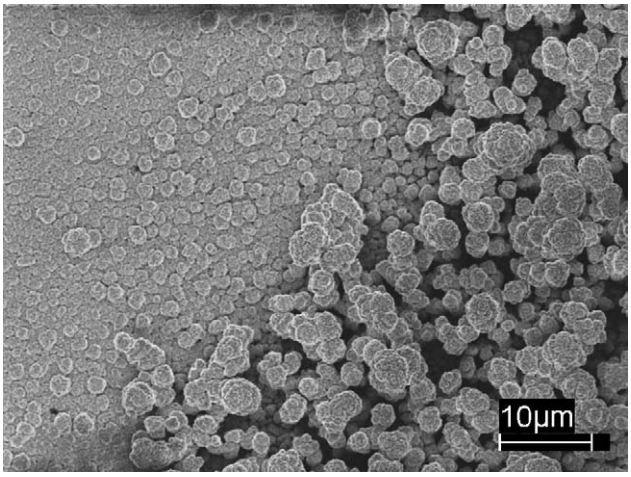

Fig. 5. SEM picture of an area situated at the edge of one of the two lobes where carbon-nanoparticles agglomerates were expelled from the quartz resonator surface, while the crystal current was 140 mA.

carbon-nanoparticles agglomerates have reached the crystal surface outside the vibrating area, close to the crystal periphery, as seen in Fig. 4.

4. Discussions

The experimental results shown here reveal the complex situation on the surface of a shear vibrating quartz resonator used in QCM applications. In the early years of the QCM it was thought that AT-cut resonators exhibit a pure shear vibration. Later, compressional waves were detected in liquids and the explanation was based on the existing velocity gradients in the contacting liquid [7]. More recently [9] the possibility for flexural vibrations was evidenced.

Using the very high accelerations developed during crystal vibration and by coating the crystal resonators with carbon-nanoparticles, it was possible to reveal that out-of-plane vibrations do really exist. The origin of the two lobes on the surface of the quartz resonator, where the carbon-nanoparticles were expelled can also be explained by extending the continuity equation from liquids to solids, taking into account the concept formulated by Frenkel [14]. He stated that there is no essential difference between liquids and solids. It is the residence time of an atom or a molecule in a certain position that makes them looking different. The continuity of properties from solids to liquids was also assumed by Maxwell [15].

It seems that the recently introduced Rupture Event Scanning (REVS^{TM}) [16–18] is based on the existence of the out-of-plane vibrations on the surface of a quartz crystal resonator. Binding forces are normal to a surface and, therefore, a force in the opposite direction is necessary to break these binding forces.

It is important to take into account the complex vibration of an AT-cut quartz crystal resonator when interpreting the experimental results obtained with QCM.

On the other hand, the very high accelerations in different directions at the crystal surface can induce changes in the morphology of the deposited film. An increased catalytic activity was already noticed [19,20].

5. Conclusions

AT-cut quartz crystal resonators exhibit both an in-plane shear vibration and an out-of-plane vibration. The out-of-plane vibration revealed on two lobes along the *X*-axis of the quartz resonator originates from the velocity gradients of the shear vibration. Even out-of-plane flexural vibrations are possible as predicted theoretically. The very high acceleration associated to the out-of-plane vibrations develops a force that expels the carbon-nanoparticles. On the other hand the in-plane, shear vibration, develops a mega-gravity acceleration that helps the sedimentation of the carbon-nanoparticles. These opposite effects must be taken into account when interpreting the experimental results obtained with QCM as a mass sensor.

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Biographies

Vasile Mihai Mecea was born in 1948 in Brasov, Romania. He graduated from the Physics department of the "Babes-Bolyai" University of Cluj-Napoca, Romania in 1972. He received his Ph.D. in 1979 on a subject concerning the use of the quartz crystal microbalance for studies on hydrogen and deuterium interaction with palladium films. In Sweden he worked for various periods as visiting scientist in the Department of Materials Chemistry at Ångström Laboratory in the University of Uppsala. He worked also in R&D at Quartz Pro in Stockholm with quartz crystals and oscillators. Now he is involved in R&D of the QCM technique at QCM lab. He has published more than 40 scientific papers, most of them in the field of the QCM. He holds four patents.

Jan-Otto Carlsson was born in 1943 in Rimforsa, Sweden. He graduated from the Chemistry Department at Uppsala University in 1968. For his Ph.D. in 1979 he carried out research in the CVD of boron. He has published more than 200 articles in the field of both thermally and photolytically activated CVD. In 1987 he became full professor of surface chemistry and since 1993 he has been professor in inorganic chemistry, all at Uppsala University.

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Mats Boman was born on 4 May 1956 in Norrköping, Sweden. He received B.Sc. in Chemistry at Uppsala University in 1984 and got Ph.D. in Chemistry also at Uppsala University in 1987. In 1996–1997 he worked as post-doctoral research fellow at Applied Physics in Johanes Kepler University in Linz, Austria. From 1987 to 1999 he was assistant professor and associate professor of chemistry at Uppsala University. Within the period 1999–2001 he was associate professor of chemistry and group leader for the Nanotechnology Group at Louisiana Technical University, Ruston. Now he is professor of inorganic chemistry at Uppsala University. He published more than 90 articles and holds four patents.