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Electrical behaviour of AT-cut quartz crystal resonators as a function of overtone number

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ABSTRACT

An investigation on the electrical behaviour of quartz resonators with fundamental frequencies up to 10 MHz was carried out by impedance analysis on several overtones. The values of the equivalent electrical components of these acoustic sensors were determined and revealed to correctly match those obtained for theoretical one-dimensional crystals. The study on different harmonics allowed to evaluate the variation of the effective vibrating area of each crystal and the effect of energy trapping intrinsic to a crystal of finite surface was then emphasized. It was also shown that the impedance behaviour is affected by the piezoelectric stiffening and the boundary conditions of real quartz resonators. These perturbing effects have a significant magnitude on the fundamental harmonic mode, and to a lesser extent on the third and fifth overtones. Besides, the theoretical models established for viscoelastic analysis of coated layers are based on the assumption that the quartz crystals are ideal with an infinite surface. For this purpose, a model was proposed for different crystals to take into account the various effects influencing both resonance frequencies and bandwidths of quartz resonators.

1. Introduction

Quartz crystal resonators vibrating in a thickness shear mode are widely used like acoustic sensors as their oscillations are extremely sensitive to any change of the acoustic properties occurring in the quartz crystal and on its surfaces. Sauerbrey [1] first found that a quartz crystal resonator can be used as a microweighing device when it operates in vacuum or in air. He showed that when a rigid thin film is stuck on the surface of a quartz crystal, the additional mass vibrates synchronously with the crystal and the change of resonance frequency Δf_m is related to the thickness increase Δh through the relation:

$$\frac{\Delta f_m}{f_r} = -\frac{\Delta h}{h_q} \tag{1}$$

where h_q is the thickness of the unloaded quartz crystal and f_r is the resonance frequency of the nth overtone. The introduction of a piezoelectrically active area enables to link the thickness to the mass and consequently to relate the decrease in resonance frequency to the added mass Δm according to the so-called Sauerbrey's relationship:

$$\Delta f_m = -n \frac{2f_0^2}{\sqrt{\rho_q \mu_q}} \Delta m \tag{2}$$

where μ_q and ρ_q are the shear modulus and the density of quartz respectively and f_0 stands for the fundamental resonance frequency of an infinite unloaded quartz crystal. It is expressed by:

$$f_0 = \frac{1}{2h_q} \sqrt{\frac{\mu_q}{\rho_q}} \tag{3}$$

In addition to microweighing experiments of rigid films under vacuum, quartz crystal resonators can operate in a fluid environment in order to determine fluid property changes. In this case, the viscous damping does not only cause losses in the quality factor but also cause a significant frequency shift. For Newtonian fluids, Kanazawa and Gordon [2] have shown that this frequency change depends on both the density ρ_{fluid} and the viscosity η_{fluid} of the fluid according to the following relationship:

$$\Delta f_\eta = -\sqrt{n} \frac{f_0^{3/2}}{\sqrt{\pi \rho_q \mu_q}} \sqrt{\rho_{fluid} \eta_{fluid}} \tag{4}$$

When a crystal coated with a thin rigid film operates in a fluid, the interference between mass and viscosity effects is negligible and the problem can be treated in an additive manner [3]. Thus,

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the shift in frequency appears as the sum of both effects:

$$\Delta f_r = \Delta f_m + \Delta f_\eta \quad (5)$$

It becomes consequently difficult to extract the mass loading and the liquid properties from measuring solely the resonance frequency shift of the quartz crystal. This drawback can be overcome by considering a second quartz crystal immersed in the same fluid but used without coating in order to determine separately the fluid effects [4]. This technique based on the addition of an uncoated quartz crystal which acts as a reference has appeared particularly convenient to measure adsorption and low solubility of gases in rigid films. It was applied for determining among other things the solubility of carbon dioxide in polymers [5]. It brings some interesting alternatives for measuring extremely low gas solubility in materials [6,7]. However, this technique was implemented so far only for rigid films but its extension to soft materials could provide the possibility for many new applications. In particular, it could lead to an interesting alternative for measuring liquid–vapour phase equilibrium in systems made up of gas and extra heavy oils for which conventional PVT techniques do not work correctly and accurately because of the diffusion times of gas into these oils. Actually, long time diffusion of gas in highly viscous liquids does not allow to reach the equilibrium conditions in reasonable time during liquid–gas phase transition experiments due to the volume of sample needed in classical PVT apparatus. Non-conventional techniques based on micro-samples must thus be designed specifically for such kind of systems.

Quartz crystal microweighing techniques can be extended to viscoelastic films [8–10]. However, the non-rigid coupling between the quartz surface and the layer as well as the dissipations due to viscous friction cause strong deviations to Sauerbrey's equation that cannot be directly used for such applications. In some cases, viscoelasticity leads to a stronger effect than mass loading and the sensor response is preferentially used to measure the viscoelastic properties of materials [11]. The non-rigid character of a viscoelastic film induces a frequency shift as well as a damping of the crystal's oscillation. Consequently, a shift in frequency measurements is not sufficient to fully characterize the acoustic response of a quartz crystal loaded with a viscoelastic layer. Another quantity must be considered in order to quantify the energy dissipation. The half-band-half-width Γ is particularly convenient for this purpose as it enables to generalise the resonance frequency in a complex quantity defined by [8,12]:

$$\tilde{f}_r = f_r + i\Gamma \quad (6)$$

whose change can be related to the acoustic impedance of the additional layer in the small load approximation [8,13]:

$$\Delta\tilde{f}_r = \Delta f_r + i\ \Delta\Gamma = \frac{if_0}{\pi Z_{cq}} Z_{layer} \quad (7)$$

where $Z_{cq} = \sqrt{\rho_q \mu_q}$ is the characteristic acoustic impedance of the quartz crystal and Z_{layer} is the acoustic impedance of the layer. For a viscoelastic layer of finite thickness, this impedance takes the following form [8,9]:

$$Z_{layer} = i\sqrt{\rho_{layer} G_{layer}}\ \tan\left(\omega\sqrt{\frac{\rho_{layer}}{G_{layer}}} h_{layer}\right) \quad (8)$$

where G_{layer} is the complex shear modulus of the viscoelastic material ($G = G' + iG''$).

Due to the form of the acoustic impedance, the frequency response of a quartz resonator loaded with a viscoelastic layer of finite thickness appears as a function of 3 unknown quantities, G', G'' and h_{layer} whose mathematical complexity impedes a direct separation of mass and viscoelasticity effects. Consequently, the addition of half-band-half-width to resonance frequency measurement does not yet provide enough experimental information to derive the thickness or the mass of a viscoelastic film from quartz crystal resonator experiments. To overcome this drawback, Lucklum and co-workers [14] proposed a very convenient method which consists in measuring separately the layer thickness by performing an additional measurement at a temperature sufficiently low so that the coating can be considered as rigid and so that the Sauerbrey's relation works properly. Unfortunately, this suitable method for shear moduli estimation cannot be adapted to gas solubility measurement as in this case, the determination of mass is above all investigated and gas solubility is a function of temperature and pressure.

Another approach was proposed by Johannsmann [15] to overcome the lack of experimental information in comparison to the number of unknowns. This second approach consists in substituting the tangent in impedance of the layer by a third order Taylor expansion. This approximation which holds when the thickness of the viscoelastic film is small leads to linear functions of the square of the overtone order n^2 for both the resonance frequency and bandwidth shifts:

$$\frac{\Delta f_r}{f_r} = -\frac{8\pi^2 f_0^3}{3Z_{cq}} \frac{m_f^3 J'_f}{\rho_f} n^2 - \frac{2f_0}{Z_{cq}} m_f = a_f n^2 + b_f \quad (9)$$

$$\frac{\Delta\Gamma}{f_r} = \frac{8\pi^2 f_0^3}{3Z_{cq}} \frac{m_f^3 J''_f}{\rho_f} n^2 = a_\Gamma n^2 \quad (10)$$

where m_f is the mass per unit area of the film and $J_f = J'_f - iJ''_f = 1/G_f$ is its shear viscoelastic compliance.

By using these equations, it becomes theoretically possible to get 3 experimental data (a_f, a_Γ, and b_f) that provide sufficient information for extracting at the same time the mass and shear moduli. Thus this second technique seems perfectly adapted for monitoring the mass change caused by dissolution in a viscoelastic film. However, these equations were obtained on the assumption that the thickness of the layer is small enough to substitute the tangent by its Taylor expansion but also on the hypothesis that the resonator is an ideal quartz crystal with a finite thickness and laterally infinite dimensions. Such a theoretical quartz crystal would present a resonance frequency proportional to the overtone number in vacuum. Unfortunately, in reality this ideal behaviour is severely affected by several phenomena such as boundary conditions of a finite crystal [16], piezoelectric stiffening [8], energy trapping [17], anharmonic resonances [18] that are intrinsic to real quartz crystal resonators. These inconvenient happenings which have a significant magnitude on the resonance frequency as well as on the dissipation may interfere or even totally hide mass and viscoelastic effects. Consequently, a precise characterization of the electrical behaviour of an unloaded real quartz crystal as a function of overtone number appears as a preliminary stage for designing a technique to measure accurately the solubility of gases in viscoelastic materials by a quartz resonator technique. With this aim in mind, we studied in this first work the electrical response of several quartz crystals with various nominal frequencies in a wide frequency range and we compared the experimental impedance spectra with the theoretical expectations. A model is then proposed to separate various effects responsible for the deviations observed between real and theoretical quartz crystals.

2. Theory

In order to model the behaviour of quartz crystal resonators as a function of overtone number, the complex resonance frequencies are used, where the real part $f_{r,n}$ is the series resonance frequency and Γ_n is the half-band-half-width [13],

$$\tilde{f}_{r,n} = f_{r,n} + i\Gamma_n \quad (11)$$