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Correlation of *in situ* and *ex situ* responses of the QCM accompanying silver deposition

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In situ and *ex situ* quartz crystal microbalance measurements were made at a 10 MHz AT-cut piezoelectric resonator. A simple test is described to determine whether immersion in a solvent affects the relationship between mass loading and frequency decrease found in air. For mass loadings produced with electrodeposited silver up to 400 μg cm^{-2}, the resonant frequencies in air and in aqueous solution were found to be linearly proportional to each other with a slope of unity at the 5% significance level.

1. Introduction

The quartz crystal microbalance (QCM) has had extensive use as a mass sensitive detector in vacuum applications [1], and has become an important tool for monitoring mass changes occurring at the crystal surface when it is immersed in a liquid [2–6]. The relationship given by Sauerbrey [7] between the measured resonant frequency change (Δf, Hz) from the base value (f_0, Hz) and the mass loading (ΔM, g cm^{-2}) of the surface of the crystal is

$$\Delta f = -(2/\rho v) f_0^2 \Delta M \qquad (1)$$

where ρ is the density of the quartz and v is the wave velocity in quartz. It has been widely assumed that this relationship holds when the crystal is submerged in a liquid. This assumption was originally confirmed experimentally by the electrochemical deposition of silver [5] on a gold coated AT-cut 10 MHz crystal. Martin *et al.* [8] presented a detailed analysis of the effect of loading the crystal by a Newtonian liquid and a thin rigid mass. They showed that mass loading only results in a frequency translation, while liquid loading results in both a frequency translation and damping of the resonance peak. Gabrielli *et al.* [9] studied the effect of electrode size upon the frequency change accompanying silver deposition on one face of a 6 MHz AT-cut quartz crystal. They found that the average sensitivity was independent of silver film thickness, but markedly dependent on the size of the piezoelectric exciting electrode. Large exciting electrodes gave the theoretical (Sauerbrey) sensitivity, but smaller exciting electrodes gave substantially less sensitivity.

Gabrielli *et al.*'s results raise two significant issues regarding *in situ* QCM measurements: (i) concerning the effect of solution when using a particular kind of crystal, and (ii) concerning whether the Sauerbrey equation applies to a particular *in situ* measurement. Although commonly (i) and (ii) are lumped together, they are two independent issues. The second point involves considerations of acoustic impedance matching (for rigid films) and viscoelastic behaviour (for nonrigid films). Here we address the 'solution effect' and show how to identify crystals which meet the theoretical criteria of Martin [8], that is, crystals whose *in* and *ex situ* responses differ only by an amount described by solvent properties. Additionally our approach identifies crystals which retain these characteristics independent of rigid mass loading.

We report a new means of treating Δf and ΔM data to isolate the effect of solvent on the *in situ* frequency response of a mass-loaded QCM. This test is free of at least two ambiguities which might arise in an *absolute* calibration [5, 9]. We emphasize that the new test is meant to validate, not replace, the conventional absolute calibration of the QCM.

First, misalignment and different radii of the two exciting electrodes lead to an uncertainty in the definition of areal density on the piezoelectrically active area. Second, absolute calibration methods require that all the mass loading be confined to the piezoelectroactive region of the crystal. Electrochemical deposition results in coating of the piezoelectroactive area plus additional electroactive area. This additional, *nonpiezoactive*, area is difficult to determine accurately following cell assembly, which usually masks an ill-determined fraction of the tab used to make electrical contact to the exciting electrode on the crystal.

Our strategy is to deposit various quantities of an elastic (rigid) nonporous material. Electrochemically deposited dense metal films (here silver) meet this requirement. One then measures the accompanying frequency changes both in solution and in air. The *in situ*/*ex situ* pairs of frequency changes are then fitted to a linear least squares line. The confidence limits of the slope allow estimating whether there is an effect of solution on the relationship between frequency and mass change. If these limits include unity, we can be confident (at the specified level) that the effect of solvent is a simple, additive one. This positive result requires that the deposited film behaves identically in the presence or absence of solvent and implies that the film is rigid and solvent free.

2. Experimental details

The electrochemical quartz crystal microbalance (EQCM) cell and associated circuitry have been described previously [5]. The 10 MHz AT-cut crystals with gold exciting electrodes (piezoelectroactive area 0.22 cm^2; 'tab' width 0.25 cm and exposed area *ca.* 0.02 cm^2; 5 μm surface finish; quartz diameter = 1.37 cm) were used as supplied by the manufacturer (catalog number 031210, International Crystal Manufacturers, Oklahoma City, OK). Solutions were prepared using a Milli-Q reagent grade water system (Millipore Corporation, Bedford, MA). Chemicals were reagent grade and used as received. A (non-cyanide) silver plating solution, described by Grebe [10], was used for depositing silver metal at the QCM electrode. The crystal was mounted on the EQCM cell described previously [5]. The cell in turn was rigidly mounted to an insulating board which plugged into the oscillator circuitry within a Faraday cage. Plugging and unplugging the board did not increase the random error in frequency determinations. All plating, washing and drying operations were conducted on the same mounted crystal.

Before silver plating, the gold working electrode was electrochemically cleaned by potential cycling in 0.2 M $HClO_4$, then rinsed with pure water. The silver was deposited galvanostatically (5 μA) in a two-electrode cell configuration from nitrogen-purged silver plating solution.

3. Results and discussion

When the crystal oscillates in solution, the 'no slip' requirement generates an oscillating layer of liquid adjacent to it. This process dissipates energy into the solution and decreases the resonant frequency of the crystal. This situation has been described in terms of crystal and solution parameters [5, 11]. More recent work [8] includes a detailed analysis of the overall response of an uncoated crystal in solution.

An experiment was performed to determine how the solution response of a mass loaded crystal differed from the gas phase response. The resonant frequency of the uncoated gold electrode on the crystal was first determined in air and in the silver plating solution. Next, silver was deposited. Then the resonant frequency of the coated crystal was determined in solution and in air. In the latter case the procedure involved unplugging the cell from the frequency board, emptying the solution from the cell, and rinsing and drying the electrode. The plating solution was returned to the cell, more silver plated, the cell replaced in the Faraday cage and the resonant frequency determinations repeated. Five pairs of frequency changes were obtained, as summarized in Table 1.

Table 1. Ex situ (Δf_{ex}) and in situ (Δf_{in}) QCM frequency changes accompanying Ag plating[‡]

Number of silver deposition steps	$-\Delta f_{ex}$*/Hz	$-\Delta f_{in}$†/Hz
1	1366	1400
2	2484	2514
3	4631	4562
4	20930	21200
5	103113	102785

* Referred to resonant frequency of the unloaded *ex situ* crystal. (*Ex situ* f_0 = 10.013 240 MHz).

† Referred to resonant frequency of the unloaded *in situ* crystal. (*In situ* f_0 = 10.000 700 MHz).

‡ Masses deposited in successive experiments were in the range 6.4 to 400 μg cm^{-2}. (Calculated from Faraday's law and the deposition charge.)

The data in Table 1 were fitted to the equation

$$-\Delta f_{\mathrm{ex}} = A - B\Delta f_{\mathrm{in}} \qquad (2)$$

by the method of linear least squares. The slope of the line, B, is 0.9965 and the intercept, A, is 80.67 Hz. The 95% confidence interval for the slope is 0.9901 to 1.0129 (0.9965 ± 0.0064) which includes unity. The 95% confidence interval for the intercept is −221 to 383 Hz (80.67 ± 302 Hz) which includes zero. Thus we can be 95% confident [12] that the *ex situ* and *in situ* resonant frequencies differ by a constant over the range of mass loadings studied (0 to 400 μg cm^{-2}). In our opinion, a statistically equivalent *absolute* measurement (plotting Δf_{in} against independently determined ΔM) would be extremely demanding.

The conclusion of the previous paragraph sheds no light on the relationship between Δf_{ex} and ΔM. For example, if there were an extremely bad acoustic mismatch between the deposited film and the substrate, and $\Delta f_{\mathrm{ex}}/f_0$ were greater than 0.01, deviations from the Sauerbrey equation would be readily detectable [1]. However, these deviations would not influence the value of B in Equation 2, because B is determined by solution properties. We note that, for our experiment, the acoustic impedance difference and $\Delta f_{\mathrm{ex}}/f_0$ are sufficiently small to allow neglecting such deviations from the Sauerbrey equation. This situation conforms with Martin's model [8] for *thin* rigid films, and we found for silver that there is only a simple translation, but not shape change, of the resonance peak.

We make three final observations. First, we chose to deposit a nonporous, solvent impermeable film. Had the rigid film been porous or had it reversibly partitioned solvent *in situ*, the plot of Equation 2 would have been linear, but a value of B greater than unity would have resulted. Second, if the viscoelastic behaviour of the film had been different *in situ* and *ex situ*, the plot of Equation 2 could not give a straight line. It is difficult to imagine a situation involving a viscoelastic film where change of medium would not affect viscoelastic characteristics. Consequently, obtaining a straight line slope would be strong evidence for rigidity; unit slope signifies the same film solvent content *in situ* and *ex situ*. Similar information concerning film rigidity in solution may be obtained using crystal impedance measurements, which require more expensive instrumentation and are no simpler to perform. Third, we find no evidence that the 5 μm surface finish of the electrode affects the mass sensitivity of the 10 MHz AT-cut crystals we use.

4. Conclusions

We have described a procedure for determining the effect of solution on the Δf response of quartz crystal oscillators. It is well suited for testing crystals having various resonant frequencies and exciting electrode materials and geometries for their suitability as EQCM sensors. The mass sensitivity of readily available gold coated AT-cut 10 MHz quartz crystals (5 μm surface finish) is not affected by contacting one face with solution; these crystals are ideally suited to EQCM experiments.

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