The Quartz Crystal Microbalance, a Versitile Characterization Tool for Thin Film Coatings

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This is the first of two articles on the use of quartz crystal microbalances (QCM). You will be impressed on what these instruments can accomplish and their applications. This first installment focuses on basics and measurement capabilities. The following article will address new applications.

WHAT ELSE CAN A QCM DO?

The first practical application of Quartz Crystal Microbalance (QCM) sensors was as thickness and deposition-rate monitors for gas phase, thin-film processing in the vacuum coating industry.

For many years, QCMs were regarded exclusively as gas-phase mass detectors; however, more recently their application has been extended since scientists realized that they can be operated in contact with liquids and viscoelastic deposits. In this case, both frequency and series resonance resistance of the quartz oscillator are important to completely characterize the material in contact with the crystal electrode.

The development of QCM Systems for use in fluids opened a new world of applications, including electrochemistry and micro-rheology. More recent developments have focused on tailoring electrode surface chemistry (i.e. specialized polymer and self-assembled coatings) so that these devices can be applied as discriminating mass detectors for:

(1) specific gas detection
(2) environmental monitoring
(3) immunosensing
(4) basic surface-molecule interaction studies.

The purpose of this article is to provide a quick overview of the many novel ways in which QCM sensors are being used for thin-film analysis, and to briefly describe the latest theoretical models used to interpret the results.

BACKGROUND

Sauerbrey was the first to recognize the potential usefulness of QCM technology and demonstrate the extremely sensitive nature of these piezoelectric devices towards mass changes at the surface of QCM electrodes. The results of his work are embodied in the Sauerbrey equation, which relates the mass change per unit area at the QCM electrode surface to the observed change in oscillation frequency of the crystal:

$$f = - C_f \cdot f_n \qquad \textbf{(equation 1)}$$

where,
   f - the observed frequency change, in Hz,
   f_n - the change in mass per unit area, in g/cm^2, and
   C_f - the sensitivity factor for the crystal used (i.e. 56.6 Hz μg^{-1} cm^2 for a 5MHz AT-cut quartz crystal at room temperature.)

The Sauerbrey equation relies on a linear sensitivity factor, C_f, which is a fundamental property of the QCM crystal. Thus, *in theory*, the QCM mass sensor does not require calibration. However, it must be kept in mind, that the Sauerbrey equation is only strictly applicable to uniform, rigid, thin-film deposits. Vacuum and gas phase thin-film depositions which fail to fulfill any of these conditions actually exhibit more complicated frequency-mass correlations and often require empirical calibration to yield accurate results.

ELECTRICAL MODEL

The Butterworth van Dyke (BVD) electrical model for a quartz crystal resonator is shown in **Figure 1**. This model is often used to represent the electrical behavior of a crystal resonator near series resonance. The model has also been useful in predicting the frequency shifts and losses of the AT-cut quartz crystal typically used in QCM applications.

The BVD electrical model consists of two arms. The **motional arm** has three series components modified by the mass and viscous loading of the crystal:

(1) R_m (resistor) corresponds to the dissipation of the oscillation energy from mounting structures and from the medium in contact with the crystal (i.e. losses induced by a viscous solution or film)
(2) C_m (capacitor) corresponds to the stored energy in the oscillation and is related to the elasticity of the quartz and the surrounding medium
(3) L_m (inductor) corresponds to the inertial component of the oscillation, which is related to the mass displaced during the vibration.

Typical values of these parameters for a 1" diameter, 5MHz quartz crystal are C_m=33fF, L_m=30mH, and R_m=10 Ω (for a dry crystal), R_m=400 Ω (for a crystal with one face in water), or R_m=3500 Ω (for a crystal with one face in 88% glycerol).

The motional arm is shunted by the **parasitic capacitance, Co**, which represents the sum of the static capacitances of the crystal's electrodes, holder, and connector capacitance.

In a QCM application the motional inductance, L_m, is increased when mass is added to the crystal electrode - the frequency shift of the series resonance is a sensitive indicator of the added mass and
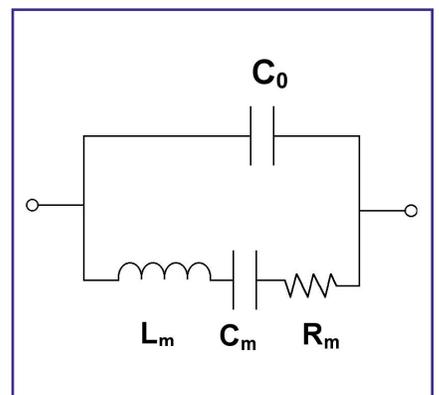

Figure 1. Butterworth-van Dyke model of Quartz Crystal Resonator.

films of less than 1ng/cm^2 can be easily resolved by a QCM. The motional resistance, R_m, can also provide important information about a process since soft films and viscous liquids will increase motional losses and so increase the value of R_m.

Accurate QCM measurements with viscous loads requires strict operation at the true series resonance frequency of the motional arm (where the reactance of Cm and Lm cancel. As a result, QCM instruments specifically developed for mass and viscocity measurements in the presence of viscous loads require dedicated circuitry to compensate against the effects of the parasitic capacitance and to provide the resistive losses at series resonance.

Gas Phase Thickness Monitor

The first use of QCMs was as mass sensors and thickness monitors in gas phase, thin-film depositions. To this date, this continues to be one of the most important areas of application for this technology.

Sauerbrey Equation

Sauerbrey's equation (equation 1) is often used to calculate mass loadings and thin-film thicknesses in vacuum depositions. The basic assumption is that the incremental change in mass from the foreign film is treated as though it were really an extension of the thickness of the underlying quartz. The foreign film is considered rigid and so thin that it does not experience any shear forces during vibration. As a result, the sensitivity factor, C_f, is a fundamental property of the quartz crystal and does not consider any of the properties of the foreign film (i.e. it is only dependent on the acousto-elastic properties of quartz.)

$$C_f = 2 \cdot n \cdot f_o^2/(\rho_q \cdot \mu_q)^{1/2} \qquad \textbf{(equation 2)}$$

where,

   n - number of the harmonic at which the crystal is driven,

   f_o - the resonant frequency of the fundamental mode of the crystal, in Hz,

ρ_q - density of quartz – 2.648 g cm^{-3},

and

μ_q - shear modulus of quartz - $2.947 \cdot 10^{11}$ g.cm^{-1}.s^{-2}

The dependence of the frequency change on the mass coverage per unit area, emphasizes the fact that, within certain limits, the sensitivity factor is independent of the electrode geometry. Thus, in theory, the QCM mass sensor does not require calibration for this application. *This ability to calculate mass loading from first principles is obviously a very active feature of these devices.*

Film thickness is often the parameter of interest in gas-phase thin-film depositions. If the mass coverage is believed to be uniform, the thickness of the film is easily calculated dividing the mass per unit area provided by Sauerbrey's equation by the material's density:

$$T_f = \Delta m / \rho_f \qquad \textbf{(equation 3)}$$

where,

   ρ_f - density of film material, in g/cm^3,

  Δm - change in mass per unit area, in g/cm^2 (calculated from Sauerbrey's equation), and

   T_f - Thickness of the film, in cm.

Z-match Method

It is generally accepted that when the mass loading from the deposit causes a change of less than 2% of the resonant frequency of the unloaded crystal, Sauerbrey's equation can be used to obtain accurate results in thin-film thickness calculations. As the thickness of the film increases, the Sauerbrey equation must be extended to incorporate the elasticity of the deposit. Lu and Lewis gave a specially simple equation (equation 4) for the calculation of the dependence of Δf on Δm, which is currently applied by most thickness monitors to calculate real-time thin-film thicknesses in gas phase depositions.

$$\Delta m = [(N_q \cdot \rho_q)/(\Pi \cdot Z \cdot f_L)] \cdot \tan^{-1}[Z \cdot \tan [\Pi \cdot (f_U - f_L)/f_U]] \qquad \textbf{(equation 4)}$$

where,

Δm - change in mass per unit area, in g/cm^2,

  N_q - Frequency Constant for AT-cut quartz crystal: 1.668*1013 Hz.Å,

ρ_q - density of quartz: 2.648 g·cm^{-3},

  ρ_f - density of film material, in g·cm^{-3},

  f_U - Frequency of unloaded crystal (prior to deposition), in Hz,

  f_L - Frequency of loaded crystal, in Hz,

  μ_q- shear modulus of quartz: $2.947 \cdot 10^{11}$ g·cm^{-1}·s^{-2},

  μ_f - shear modulus of film material, and

Z: Z-Factor of film material = $[(\rho_q \cdot \mu_q)/(\rho_f \cdot \mu_f)]^{1/2}$**.**

This analysis of frequency changes including the acoustic impedances of the quartz and film is often called the "Z-match" method. The accuracy of the mass load and film-thickness calculation is often limited by how well the Z-Factor and density of the material are known. Density and Z-Factor values are typically very close to bulk values. The bulk density and shear modulus values for common film materials can be found in many material reference handbooks.

The Lu and Lewis equation is generally considered to be a good match to the experimental results for frequency changes up to 40% (relative to the unloaded crystal). Keep also in mind that the Z-match equation strictly applies to "rigid" deposits. Films which behave viscoelastic, such as organic polymer films and self assembled monolayers with large thickness or viscoelasticity, will exhibit significant deviations from both equations 1 and 4.

Crystal failures are also often experienced before a 40% shift in frequency is reached. Common problems are:

(1) shorts in the crystal electrodes due to excessive buildup,

(2) mode hopping to other (anharmonic) resonant frequencies due to the buildup of composite resonant modes ,

(3) deviations from theory due to fringing electrode fields developed between the electrodes and the film,

(4) unexpected shifts in fundamental frequency due to stress build up on the crystal surface,

(5) spitting of source material resulting in non-uniform films, etc.

Recent improvements in vacuum QCM technology have involved the development of new crystal coatings and materials, capable of minimizing the effects of stress build-up, electrode adhesion failures during depositions and capable of operation at higher temperatures. Successful approaches include aluminum alloy crystal electrodes, new crystal cut orientations and GaPO4 crystal material.

Liquid Viscometer

Until recently, its was believed that excessive viscous loading would prohibit operation of QCM crystals in liquids. In fact, operation in liquids is indeed possible, and the response of the quartz crystals is still extremely sensitive to mass changes at the solid-solution interface. For many years, QCMs have been used in direct contact with liquids and/or viscoelastic films to assess changes in mass and viscoelastic properties during chemical and electrochemical surface processes.

When the QCM comes in contact with a solution, there is a decrease in frequency that is dependent upon the viscocity and the density of the liquid. A quantitative understanding of the resonator behavior is a prerequisite for proper interpretation of experimental results under total liquid immersion. This problem was first treated by Glassford, and later by Kanazawa and Gordon.

Kanazawa's treatment of the influence of the solution properties on the crystal (equation 5) permits the prediction of the change in resonance frequency which accompanies immersion of the crystal into a viscous medium:

$$\Delta f = -f_U^{3/2} [(\rho_L \eta_L)/(\pi \rho_q \mu_q)]^{1/2} \quad \textbf{(equation 5)}$$

where,

f_u - frequency of oscillation of unloaded crystal,

ρ_q - density of quartz – 2.648 g·cm⁻³,

μ_q - shear modulus of quartz- 2.947·10¹¹ g·cm⁻¹·s⁻²,

ρ_L - density of the liquid in contact with the electrode, and

η_L - viscosity of the liquid in contact with the electrode.

Viscous coupling of the liquid medium to the oscillating crystal surface results not only in a decrease in the series resonant frequency but also in damping of the resonant oscillation- the viscous loss is manifested as an increase in series resonance resistance, R, of the QCM resonator. Thus, R, serves as an excellent independent measure of viscous loading by the medium (i.e. liquid or soft-film) at the crystal's surface.

> Δf and ΔR measurements are both routinely used as independent indicators of mass loading and viscosity at the crystal-liquid interface of the QCM resonator during chemical and electrochemical depositions in solution.

In a separate study, a Butterworth-Van Dyke equivalent circuit model (**Figure 1**) was applied to derive a linear relationship between the change in series resonance resistance, ΔR, of the quartz oscillator and $(\rho_L \eta_L)^{1/2}$ under liquid loading:

$$\Delta R = [n \cdot \omega_s L_U / \pi][(2 \cdot \omega_s \rho_L \eta_L)/(\rho_q \mu_q)]^{1/2} \quad \textbf{(equation 6)}$$

where,

ΔR - change in series resonance resistance, in Ω

n - number of sides in contact with liquid,

ω_s- angular frequency at series resonance(= 2·πf_s, where f_s is the oscillation frequency in solution in Hz), and

L_U - Inductance for the unperturbed (i.e. dry) resonator, usually in mH.

Several research grade QCM systems, specifically designed for operation under heavy viscous loading, are commercially available. Most modern instruments provide both frequency and resistance change signals and will typically maintain oscillation up to a series resonance resistance of about 5 KΩ (i.e. it will support crystal operation in highly viscous solutions up to 88% (w/w) glycerol in water). Some high end models provide multiple frequency operation and sophisticated software packages for data interpretation.

Excellent agreement between the frequency and resistance calculations and the experimental results has been demonstrated, making the QCM an excellent tool for the evaluation of fluid properties. Application examples include in situ monitoring of lubricant and petroleum properties. The tight correspondence between theory (equations 5 & 6) and experiment is clearly illustrated by **Figure 2**. Several viscometers, based on QCM sensing technology, are commercially available.
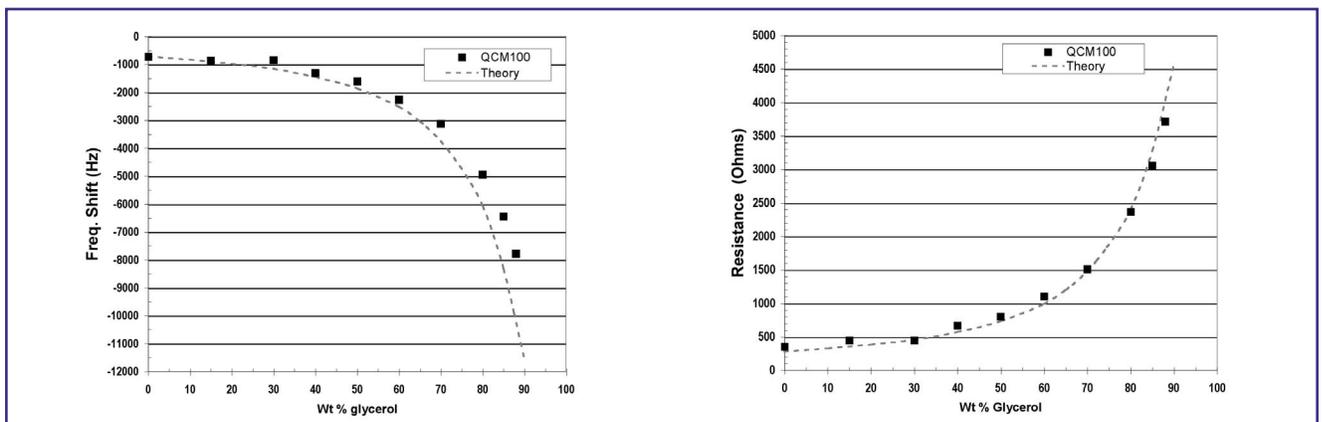

Figure 2. Frequency Shift (Hz) and Resistance Shift (Ohms) versus glycerol weight percentage (in water) as predicted by theory and as measured with a 5 MHz polished QCM crystal.
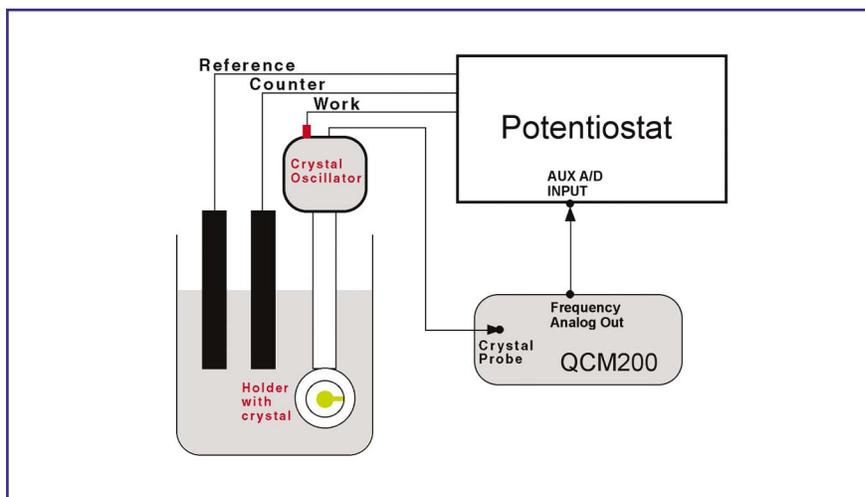
Figure 3. Basic EQCM setup

QCM crystals coated with pharmaceutical formulations are immersed in liquid solutions and used to perform real time dissolution kinetics studies.

QCM crystals in contact with individual liquid drops can also be used to characterize important properties such as surface tension of new materials with most application in the fields of lubricants and surfactants formulation.

Electrochemical QCM (EQCM)

In most electrochemical experiments, mass changes occur as material is deposited or lost from the "working" electrode. It is of interest to monitor those changes simultaneously with the electrochemical response, and the QCM is the standard means of doing so. As a gravimetric probe, the QCM has been used in many types of electrochemical studies, including: underpotential deposition of metals, corrosion, oxide formation, dissolution studies, adsorption/desorption of surfactants and changes in conductive polymer films during redox processes.

A schematic diagram of the apparatus for electrochemical quartz crystal microbalance (EQCM) experiments is given in **Figure 3**. In this example, a QCM crystal is mounted on a Crystal Holder with only one electrode exposed to the conductive solution. The Crystal Holder is connected to a Crystal Oscillator, and the liquid-contact electrode is connected to the "working electrode" lead of the potentiostat.

The Frequency Analog Out signal of the QCM controller is connected to the Ext A/D Input of the potentiostat. The potentiostat digitizes the voltage signal, and its PC software displays the Relative Frequency changes in synchronicity with the electrochemical data.

With the setup of **Figure 3**, a typical cyclic voltammetric-EQCM experiment would involve the application of the electrochemical waveform to the working electrode and the simultaneous measurement of the current flowing through the electrochemical cell and the oscillation frequency and series resonance resistance of the crystal.

Figure 4 is an example of a typical voltammogram-massogram plot obtained from a 10 mM solution of $CuSO_4$ in 0.1 M $H_2 SO_4$, using a 1 inch diameter, Au coated, quartz crystal mounted in a standard Crystal Holder as the working electrode. (Note: cathodic current is treated as positive)

The mass sensing capabilities of the QCM sensor are complemented by its ability to simultaneously detect subtle changes in the viscous loading of the quartz crystal during redox processes.

Calibration

It has been amply demonstrated in the literature that when experiments involve only relative frequency shifts which are measured in a fixed solution, the offset caused by the viscous loading of the liquid, has negligible effect on the accuracy of the Sauerbrey equation for the determination of small mass changes in rigid deposits. Quantitative interpretation of the EQCM data in those cases is based on the combination of the Sauerbrey equation (equation 1) and Faraday's law. The former relates change in frequency to change in mass for *thin, rigid deposits*, whereas the latter relates charge passed in an electrochemical experiment to the number of moles of material electrolyzed. Therefore, frequency changes can be related to the total charge passed.

An example would be the electrode-position of Ag on a Pt electrode QCM crystal. The charge, Q, is an integral measure of the total number of electrons delivered at the interface during the reduction process. To the extent, that
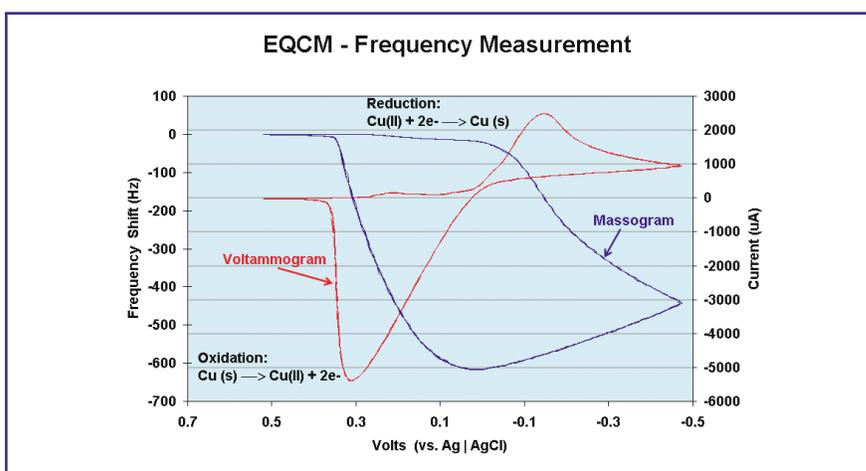

Figure 4. Cyclic voltammogram and massogram data for Cu deposition on a Au electrode. The frequency–potential diagram shows a frequency decrease in perfect sync with the deposition of Cu metal (reduction) on the crystal's surface.

each electron supplied results in the deposition of one atom of Ag, there should be a linear relationship between Q and δf as is given by equation 7:

$$\delta f = 10^6 \cdot M_w \cdot C_f \cdot Q / (n \cdot F \cdot A) \quad \textbf{(equation 7)}$$

where,

δf - frequency change, in Hz,

M_w - apparent molar mass of the depositing species, in grams/mole,

C_f - Sauerbrey's sensitivity factor for the crystal used (see equation 1),

Q - integrated charge during the reduction, in Coulomb,

A - Active deposition area of the working (i.e. liquid contact) electrode, in cm^2,

F - Faraday's constant: $9.648 \cdot 10^4$ Coulomb/mole, and

n - number of electrons transferred to induce deposition (i.e. n =1 for Ag deposition).

(The factor of 10^6 provides for the unit conversion from mg in C_f
to g in M_w.)

A plot of "δf vs Q" will deliver the apparent mass per electron of the deposited species, when n is taken into account. This is often used to elucidate the mass changes that accompany redox processes, and hence is very useful for characterizing the mechanisms of electron-transfer reactions.

However, before any calculations can be performed based on equation 7, the EQCM must be calibrated in order to properly derive:

(1) the proportionality constant, Cf, of the Sauerbrey equation in solution
(2) to account for the effective area of the working electrode.

This is generally done using a well behaved electrochemical reaction- typically electrodeposition of silver, copper or lead on a Au or Pt electrode.

Polymer Modified Electrodes

The EQCM has been extensively used to study polymer modified electrodes, particularly as a gravimetric tool to follow redox processes. However, for a linear frequency-to-mass relationship (i.e. equation 7) to hold true, the polymer overlayer must exhibit no changes in rigidity during the electrochemical process. Otherwise the viscoelastic changes will also contribute to the frequency change, leading to an erroneous interpretation of the mass changes. As a consequence, it is essential to determine whether or not viscoelastic properties of the polymer film influence the frequency measurement during polymer film experiments!

A straight forward way to detect changes in film viscoelastic properties of redox films is to simultaneously monitor the series resonance resistance, R, of the quartz oscillator during the electrochemical experiment. Some theoretical models, based on the simultaneous measurement of δf and δR, have been discussed in the literature for the extension of EQCM gravimetric measurements to non-rigid films. ■