D4.0 Quartz Monitors and Microbalances

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D4.0.0 INTRODUCTION

The quartz deposition monitor provides a sensitive, real-time means for monitoring film thicknesses during deposition. It is useful for many different deposition materials, and can be adapted to a wide variety of deposition chamber geometries. It is called a quartz monitor since a quartz crystal microbalance (QCM) is located in the sensor head. The QCM consists of a thin wafer of quartz, portions of whose two major faces have been pre-deposited with metal-film electrodes. Since quartz is a piezoelectric material, it responds to applied voltages with mechanical motion. If a free-running rf voltage is applied to the crystal, it will respond by oscillating at its natural resonant frequency, which is determined by the crystal's thickness and crystalline orientation (figure D4.0.1). Commercial crystals are cut so as to oscillate in a shear mode with resonant frequencies usually near 5 or 6 MHz. The resonant frequency decreases whenever material is deposited onto the microbalance, and the shift in frequency is directly proportional to the additional mass. Through a knowledge of the deposition material's density, the mass can then be converted to an equivalent

Figure D4.0.1. (a) A quartz crystal in the thickness shear mode of oscillation. (b) AT-cut and (c) BT-cut quartz crystal plates.
film thickness. A quartz monitor can be adapted for use with most materials, with routine sensitivities of tenths of a monolayer or better.

QCMs are classified according to the way the wafer is cut relative to the natural crystallographic orientation of quartz. The type of cut that is most commonly used is the AT-cut, with a low-temperature dependence of its resonant frequency when the crystal is at room temperature. Different thermal properties can be obtained by choosing a different type of cut, such as a rotated AT-cut, a BT-cut, or a stress-compensated (SC) cut.

In the thin film deposition limit, the frequency shift $\delta f$ is related to the thickness $d$ of material deposited onto one side of the crystal as [1]

$$d = \frac{\rho_0 v_0 \delta f}{2 \rho f^2} \quad \text{(D4.0.1)}$$

where $f$ is the initial resonant frequency, $\rho$ is the film density, $\rho_0$ the density of quartz, and $v_0$ the velocity of sound in quartz. The quantity $\rho v$ is referred to as the acoustic impedance, with $\rho_0 v_0 = 8.84 \times 10^5$ g/(cm$^2$ s) for an AT-cut crystal. Equation (D4.0.1) is valid only for small $\delta f/f$, and only so long as the total frequency shift $\Delta f$ (as measured from the bare quartz crystal resonant frequency $f_0$) is small compared to $f$. When $\Delta f/f$ becomes appreciable (i.e. when the total accumulation of material is a non-negligible fraction of the mass of the quartz crystal), corrections must be made to equation (D4.0.1) to restore its accuracy (see section D4.0.3).

### D4.0.1 EQUIPMENT AND SET-UP CONSIDERATIONS

Quartz crystals for commercial rate monitors are typically about $1/4''$ in diameter, with a portion of the central region fully plated on both sides. It is this region which oscillates [2] and the only part that need be exposed to the deposition source. The crystal is mounted within a sensor head which supplies both electrical contacts and mechanical support. Sensor heads are commercially available in a variety of shapes and sizes, with diameters typically no larger than twice that of the crystal's. Figure D4.0.2 shows a typical sensor head for a QCM. The sensor head is supported by two liquid feedthroughts for cooling water, and the assembly includes an electrical contact wire. The compact size of the sensor allows for convenient placement with minimal system modification or expense.

The most obvious placement of the sensor head is immediately adjacent to the sample so as to receive an equivalent amount of deposited material. It can, however, be placed nearly anywhere which is in range of the deposition source, with only a slight decrease in accuracy. In the latter case, the monitor must be calibrated with respect to the target position. This generally needs to be done but once for any given geometry and deposition method. It entails putting a second quartz monitor in place of the sample for a trial deposition. By comparing the thicknesses of the films deposited on each monitor, one can determine the ratio of deposition rates for the two positions. The decrease in accuracy mentioned earlier arises because this ratio will fluctuate slightly during the course of a deposition. One can determine the magnitude of the fluctuations by making several calibration runs, but one cannot precisely predict how the ratio will fluctuate during a single deposition. One advantage to placing a monitor in a position where less material falls upon it is that the effective lifetime of the monitor is extended.

The external hardware for the quartz monitor consists of an oscillator circuit and frequency-counting electronics. Commercial systems are available with a wide range of sophistication. These systems will automatically convert frequency shift to equivalent film thickness and deposition rate, employing density and acoustic impedance parameters supplied by the user. On the opposite end of the spectrum, one can directly monitor the frequency shift of a home-built oscillator circuit (for example, figure D4.0.3) [3] which has been attached to a separately purchased sensor head, and convert frequency shift to film thickness via equation (D4.0.1) or (D4.0.2).
D4.0.2 QCM OPERATING CONSIDERATIONS

Quartz-crystal Life Expectancy

As the deposition material accumulates, equation (D4.0.1) becomes progressively less accurate, and the crystal becomes increasingly difficult to set into oscillation. There are a number of ways to increase the effective life of the monitor which incur minimal loss of accuracy. One approach is to reduce the quantity of deposited material by placing the sensor head in a position where the deposition rate is some (calibrated) fraction of the rate at the target position. A shutter can alternatively be installed on the sensor head, and opened only so often as is necessary to verify the deposition rate. Sensor heads with externally controlled shutters are commercially available, as well as heads which contain more than one quartz crystal.

Irrespective of its mounting geometry, a crystal's material accumulation will eventually reach a level where
Figure D4.0.3. Clapp oscillator circuit diagram. The output is taken across the 100 Ω resistor.

A modified form of equation (D4.0.1) becomes necessary:

\[ d = \frac{\rho_v \nu_v \Delta f}{2 \rho} \left[ 1 + \left( \frac{\delta f}{f} \right) + \frac{\pi^2}{3} (1 - Z^2) \left( \frac{\Delta f}{f} \right)^2 \right]. \]  

We emphasize that \( \Delta f \) is the total change in frequency of the QCM, accumulated over the life of the crystal, while \( f \) is the resonant frequency at the start of a particular deposition. The Z-factor is given by the ratio of the acoustic impedance of the deposition material to that of the quartz:

\[ Z = \frac{\rho_v}{\rho_q \nu_q} \]  

where \( \nu \) is the velocity of sound in the film material. The reader is referred to reference [1], p 49, for a discussion of accumulations involving multiple materials with different Z-factors.

Temperature of the Operating Environment

In addition to the massload dependence, the resonant frequency is also dependent to various degrees on temperature, pressure and stresses presented by the deposited or adsorbed film. For example, a 5 MHz crystal will oscillate near 4.995 MHz when cooled to 77 K. The mass sensitivity itself is not greatly affected by the environmental operating temperature, but temperature effects can reduce the accuracy of the QCM by causing non-mass-related changes in the resonant frequency.

The temperature of the monitor generally increases upon exposure to the incoming deposition material. Commercial quartz crystals are designed to operate at room temperature and are therefore cut at an angle which results in a zero ‘temperature coefficient’ \( \delta f/\delta T \) at room temperature. In many cases, however, the temperature will rise during the deposition to a point where its effect on frequency cannot be neglected. Liquid feedthroughs are standard on commercial rate monitor heads to allow cooling of the sensor head during deposition. If water cooling of the sensor head is unavailable or undesirable, then the head can be heat-sunk with a thermally conducting material. The sink should consist of a material such as copper or aluminium, and should link the head to a chamber wall or other item which is not easily warmed. If monitor heating effects remain problematic, one should relocate the sensor head to another position, or else let the QCM heat up while the material is being deposited, and take the thickness reading after the deposition has ceased and the QCM temperature has returned to room temperature.

The above discussion applies to QCMs operated at room temperature. Crystalline quartz undergoes a phase transition at 573 °C, and clearly cannot be operated above this temperature. QCMs can be operated at low temperature, with \( AT \)-cuts being more stable at 4 K than at room temperature. The \( AT \)-cut crystal exhibits a rather high temperature coefficient at liquid-nitrogen temperatures however, and a specially cut crystal...
(one that is insensitive to temperature fluctuations at that different temperature) may be desired for greater stability.

We note that if the crystal is heated during deposition, what are essentially changes in the elastic constant of the QCM can lead to changes in the resonant frequency. These changes can occur spontaneously within the course of a deposition, appearing as abrupt shifts in the frequency. They usually amount to less than a few Å error in the calculated thickness, which is negligible for most applications.

**Film Stress Effects**

When stresses are presented to the faces of the quartz oscillator, changes in the elastic properties of the quartz produce a shift in the resonant frequency. The magnitude of a stress-induced frequency shift can range from being undetectable to providing a dominant source of frequency shift. Adopting the convention that a positive lateral stress $T_l$ corresponds to film tension, then the frequency shift due to film stress effects is given by [4]:

$$\frac{\delta f_s}{f_0} = -2.75 \times 10^{-11} T_q - \frac{T_s}{t_q} \int_0^{t_l} T_l \, dx$$

(D4.0.4)

where $t_q$ and $t_l$ are the respective quartz crystal and film thicknesses in metres and $T_s$ is the average lateral stress, in N/m², arising from the presence of the film. The lateral stress induced by a liquid-nitrogen monolayer on a flat gold surface electrode has been measured by means of a double-oscillator (AT/BT) technique [5], and was found to produce a positive frequency shift of the order of 2 Hz. The stress term was observed to be far less significant (with respect to the mass-loading term) for higher film coverages. Stress effects may be dominant during ion bombardment of surfaces to remove material, during the formation of oxide films, and for certain deposition conditions which result in porous films. As an initial test to determine whether stress effects are significant, one can use AT-cut crystals of two different frequencies. If they do not yield the same film thickness, then stress effects may well be present. If so, a combined AT–BT cut monitor may be required. AT- and BT-cut crystals can be selected which exhibit equal mass-loading frequency shifts, but opposite stress frequency shifts, so that simultaneous solution of two equations describing frequency shift will yield the true shift due to mass deposition (see reference [1], chapter 4).

**Film Density and Adhesion Considerations**

Because the QCM measures mass rather than thickness, any material with an ill-defined density, such as a porous film or alloy, can be problematic. Problems can also arise if the material being deposited fails to adhere properly to the electrode surface. In the latter case, the difficulty can sometimes be remedied by first depositing an overlayer of some third material, which interacts in a more desirable way with the deposition material. Commercial QCMs are usually plated with silver or gold, which are suitable for most materials whose deposition one might wish to monitor. Commercial systems are available which can handle alloy depositions. Porous materials remain problematic for the QCM, if one truly requires the thickness of the film rather than its mass.

**Environmental Pressure Effects**

Gas pressure effects are negligible in the vast majority of vapour-deposition conditions. Nonetheless, for completeness we note that the resonant frequency of the quartz has a dependence on the gas pressure surrounding it, described by the relation [6]:

$$\frac{\delta f_p}{f_0} = -0.72 \times 10^{-6} \sqrt{\pi \rho_g \eta_g f_0} + (18.35 - 0.015 T) \times 10^{-10} P.$$  

(D4.0.5)

The pressure is in units of Torr, the gas viscosity and mass density, $\eta_g$ and $\rho_g$, are in cgs units, and the temperature $T$ is in Kelvin. The first term arises from the viscous drag of the gas on the crystal while
the second term reflects a change in elastic constants of the quartz due to hydrostatic pressure. The gas pressure contribution to the frequency shift near monolayer completion for a nitrogen gas at 150 Torr is \( \approx 1-2 \) Hz for a 6 MHz crystal.

D4.0.3 NON-STANDARD OPERATING ENVIRONMENTS

The above discussion has focused on deposition of solid films in vacuum environments. QCMs have been utilized for vacuum erosion studies [7] as well as to monitor film deposition in electrochemical liquid environments [8, 9]. They have moreover been routinely utilized to monitor liquid film deposits [10, 11] and gas uptake rates. In order to study whether the surface electrode (or a film deposited on it) is rough, fractal, or porous, the monitoring of liquid adsorbate uptake is particularly useful [12, 13]. By simultaneously measuring the amplitude and frequency of oscillation, QCMs have been used to probe dynamical properties of the film [14].

REFERENCES