QUARTZ CRYSTAL MICROBALANCE

Definition

A **quartz crystal microbalance (QCM)** is a device that measures a mass per unit area by measuring the change in frequency of a quartz crystal resonator.

Basics

The resonance is disturbed by the addition or removal of a small mass due to oxide growth/decay or film deposition at the surface of the acoustic resonator. The QCM can be used under vacuum, in gas phase ("gas sensor", first use described by) and more recently in liquid environments. It is useful for monitoring the rate of deposition in thin film deposition systems under vacuum. In liquid, it is highly effective at determining the affinity of molecules (proteins, in particular) to surfaces functionalized with recognition sites. Larger entities such as viruses or polymers are investigated, as well. Frequency measurements are easily made to high precision (discussed below); hence, it is easy to measure mass densities down to a level of below 1 μg/cm2. In addition to measuring the frequency, the dissipation is often measured to help analysis.

The dissipation is a parameter quantifying the damping in the system, and is related to the sample's viscoelastic properties.

Quartz is one member of a family of crystals that experience the piezoelectric effect. The piezoelectric effect has found applications in high power sources, sensors, actuators, frequency standards, motors, etc., and the relationship between applied voltage and mechanical deformation is well known; this allows probing an acoustic resonance by electrical means. Applying alternating current to the quartz crystal will induce oscillations. With an alternating current between the electrodes of a properly cut crystal, a standing shear wave is generated. The Q factor, which is the ratio of frequency and bandwidth, can be as high 106. Such a narrow resonance leads to highly stable oscillators and a high accuracy in the determination of the resonance frequency. The QCM exploits this ease and precision for sensing. Common equipment allows resolution down to 1 Hz on crystals with a fundamental resonant frequency in the 4 – 6 MHz range. A typical setup for the QCM contains water cooling tubes, the retaining unit, frequency sensing equipment through a microdot feed-through, an oscillation source, and a measurement and recording device.

The frequency of oscillation of the quartz crystal is partially dependent on the thickness of the crystal. During normal operation, all the other influencing variables remain constant; thus a change in thickness correlates directly to a change in frequency. As mass is deposited on the surface of the crystal, the thickness increases; consequently the frequency of oscillation decreases from the initial value. With some simplifying assumptions, this frequency change can be quantified and correlated precisely to the mass change using Sauerbrey's equation. Other techniques for measuring the properties of thin films include Ellipsometry, Surface Plasmon Resonance (SPR) Spectroscopy, and Dual Polarisation Interferometry.

Gravimetric and Non-Gravimetric QCM

The classical sensing application of quartz crystal resonators is microgravimetry. Many commercial instruments, some of which are called thickness monitors, are available. These devices exploit the Sauerbrey relation. For thin films, the resonance frequency is – by-and-large – inversely proportional to the total thickness of the plate. The latter increases when a film is deposited onto the crystal surface. Monolayer sensitivity is easily reached. However, when the film thickness increases, viscoelastic effects come into play.

In the late 80’s, it was recognized that the QCM can also be operated in liquids, if proper measures are taken to overcome the consequences of the large damping. Again, viscoelastic effects contribute strongly to the resonance properties.

Today, microweighing is one of several uses of the QCM. Measurements of viscosity and more general, viscoelastic properties, are of much importance as well. The “non-gravimetric” QCM is by no means an alternative to the conventional QCM. Many researchers, who use quartz resonators for purposes other than gravimetry, have continued to call the quartz crystal resonator “QCM”. Actually, the term "balance" makes sense even for non-gravimetric applications if it is understood in the sense of a force balance. At resonance, the force exerted upon the crystal by the sample is balanced by a force originating from the shear gradient inside the crystal. This is the essence of the small-load approximation.

Crystalline α–quartz is by far the most important material for thickness-shear resonators. Langasite (La3Ga5SiO14, “LGS”) and gallium-orthophosphate (GaPO4) are investigated as alternatives to quartz, mainly (but not only) for use at high temperatures. Such devices are also called “QCM”, even though they are not made out of quartz (and may or may not be used for gravimetry).

Surface Acoustic Wave Based-Sensors

The QCM is a member of a wider class of sensing instruments based on acoustic waves at surfaces. Instruments sharing similar principles of operation are shear horizontal surface acoustic wave (SH-SAW) devices, Love-wave devices, and torsional resonators. Surface acoustic wave-based devices make use of the fact that the reflectivity of an acoustic wave at the crystal surface depends on the impedance (the stress-to-speed ratio) of the adjacent medium. (Some acoustic sensors for temperature or pressure make use of the fact that the speed of sound inside the crystal depends on temperature, pressure, or bending. These sensors do not exploit surface effects.) In the context of surface-acoustic wave based sensing, the QCM is also termed "bulk acoustic wave resonator (BAW-resonator)" or "thickness-shear resonator". The displacement pattern of an unloaded BAW resonator is a standing shear wave with anti-nodes at the crystal surface. This makes the analysis particularly easy and transparent

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