# QCM-D from QSense

QSense
[ Together with Biolin Scientific ]
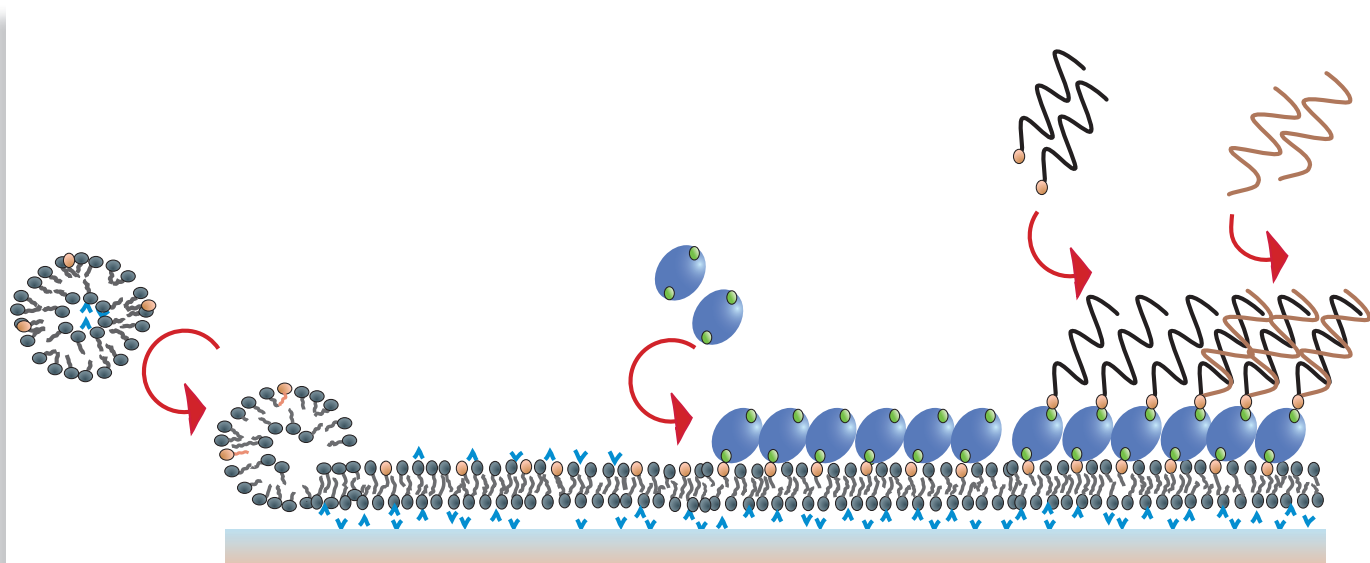
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## A1 History

This short history lesson about the QCM-D technique is mainly based on the doctoral thesis by Rodahl [1]. The discovery of the piezoelectric effect is attributed to Pierre and Jacques Curie. In 1880, they showed that crystals of Rochelle salt could produce electricity when pressure was applied in certain crystallographic directions [2]. But it was not until the end of the 1950s that this phenomenon started to be investigated systematically. In 1959 Sauerbrey published a paper that showed that the frequency shift of the QCR was proportional to the added mass [5]. This paper marks the birth of a new quantitative tool to measure very small masses: the Quartz Crystal Microbalance, QCM. For a start, measurements were all performed in vacuum or in gas phase. Several investigators have considered the use of the resonator in liquid media, but have not investigated it further since they thought that liquids would completely dampen the mechanical oscillation. But after Nomura et al. [15] showed that a crystal completely submersed in a liquid could be excited to stable oscillation many new applications became possible for the QCM.

A new group of 'wet' researchers started to use the QCM after the reports by Nomura et al. The most common use (in terms of the number of publications) of the QCM in the liquid phase has been in electrochemistry as a tool to measure interfacial processes at electrode surfaces. The QCM is now routinely used in many electrochemical experiments and is known as the Electrochemical Quartz Crystal Microbalance, EQCM. Rodahl explored in his doctoral thesis [1] not only the resonant frequency of a QCM but also the dissipation factor, D. This combination of f and D opened up a variety of new application areas. It was now possible to measure not only how much mass that is added to the crystal, but also if the material is stiff or viscoelastic and/or if the material passes through a structural change. Measurements on biochemical systems [16] and cell adhesion systems [17, 18] with information about the conformational changes were now also possible and explored by Höök in his Ph.D. thesis [16]. The viscoelasticity is also an important property in polymer science. Only a few articles have been found where the technique is used on polymer films [19, 20]. Physicists who have been familiar to the technique have mainly performed these studies but as the technique becomes more known new polymer- and biochemistry-research groups continuously start exploring its possibilities.

## A2 Theory
### Piezoelectric resonators

In principle all piezoelectric material can be used to make a piezoelectric microbalance. However the most commonly used is $\alpha$-quartz (hereafter only referred to as quartz), which is a crystalline stable form of silicon dioxide, $SiO_2$, to temperatures up to 573 °C (see Figure A.1). Quartz crystals are comparatively cheap and easy to produce. This is why they are so commonly used.
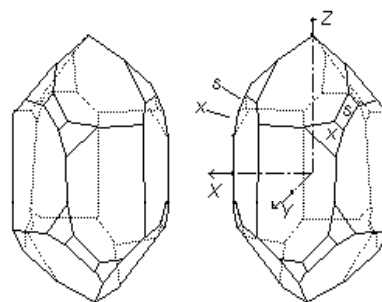


Figure A.1. The natural faces of the left and righthanded $\alpha$-quartz. The Z-axis is parallel to the trigonal axis and the X-axis is parallel to one of the digonal axes. The Y-axis is then chosen so that a right-handed rectangular coordinate system is formed.

The crystal can be cut in numerous ways. The X-cut was the first used. When the crystal is cut in this way the oscillation is parallel to the electric field. A major drawback for this cut is that the resonant frequency becomes very temperature dependent.
In 1934 the AT-cut was introduced. By slightly varying the cut angle $\theta$, it is possible to obtain close to zero temperature-dependence of the resonant frequency at a desired temperature between -60 to 100 °C (and even outside this range) (see Figure A.2). The oscillation in the AT-cut is perpendicular to the electric field as schematically shown in Figure A.3.
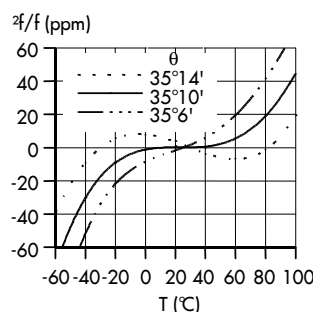


Figure A.2. The resonant frequency dependence on temperature and the cut angle $\theta$.

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## Electrodes

The electric field is applied by depositing a pair of electrodes, for example by evaporation or sputtering, directly onto the major faces of the quartz plate (see Figure A.4). The thickness of the electrodes is usually around 100 nm.

Basically any electrically conducting material that can be applied to the quartz can be used as electrodes. The most common electrode materials are Al, Ag, and Au.

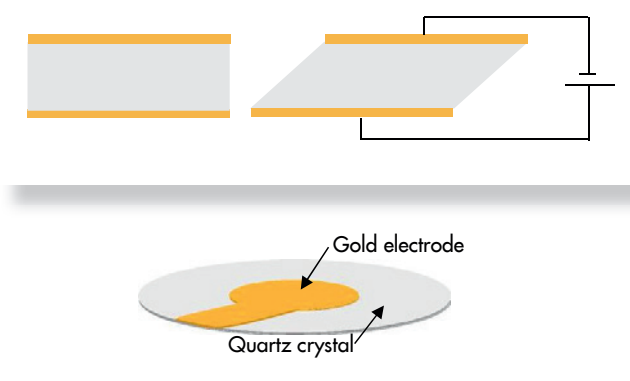Figure A.3. A schematic illustration of the strain induced in an AT-cut crystal.



Figure A.4. A crystal with its electrodes.

## Mass sensitivity

Sauerbrey proposed a simple physical model for the observed proportionality between added mass and induced frequency shift [5]. By defining the area density of quartz as $m_q = t_q \rho_q$, where $\rho_q$ and $t_q$ are the density and thickness of the quartz plate, respectively he obtained

$$f = \frac{n v_q \rho_q}{2 m_q}$$

(Equation 2.1)

where n is the number of waves and $v_q$ is the wave velocity in the crystal plate. By differentiating equation 2.1 he obtained

$$df = -\frac{f}{m_q} dm_q$$

(Equation 2.2)

Sauerbrey made the assumption that for small mass changes, the added film can be treated as an equivalent mass change of the quartz crystal itself. By making the substitution D ➜ Δ, the equation can therefore be written

$$\Delta f = -\frac{f}{m_q} \Delta m = -\frac{f}{t_q \rho_q} \Delta m = -\frac{n}{C} \Delta m$$

(Equation 2.3)

where $\Delta m = \rho_f t_f$, $\rho_f$ and $t_f$ are the density and thickness of the added film, respectively, and C is the so-called mass sensitivity of the QCM. Equation 2.3 has become known as the Sauerbrey equation.

For an AT-cut quartz crystal, where $\rho_q$=2650 kg/m³ and $v_q$=3340 m/s [2], the mass sensitivity for a 5 MHz resonator oscillating in its fundamental mode is 17.7ng x cm⁻² x Hz⁻¹ (observe that n=3 for the third overtone (15 MHz)). This means that the addition of one monolayer of water, which has an area density of approximately 0.25 mg/m², causes a frequency shift of -1.4 Hz. Since the resonant frequency of a 5 MHz crystal resonating in vacuum can easily be measured with a precision of 0.01 Hz, very small masses can be measured. Equation 2.3 is valid if the added mass is:

- small compared to the weight of the crystal
- rigid
- evenly distributed over the active area (see figure 2.5) of the crystal

Sauerbrey, in his continued investigation of the mass sensing properties of the QCM, showed that the crystal vibration is restricted to the area where the electrodes overlap as illustrated in figure A.5 [17]. This area of vibration is called the active area of the crystal.

The amplitude of vibration, A(r), peaks in the center of the electrode r = 0 and tapers off in a Gaussian fashion towards the edges of the electrodes, as illustrated in Figure A.5. The maximum amplitude A(r)$_{max}$ is about 1 to 10 ηm.
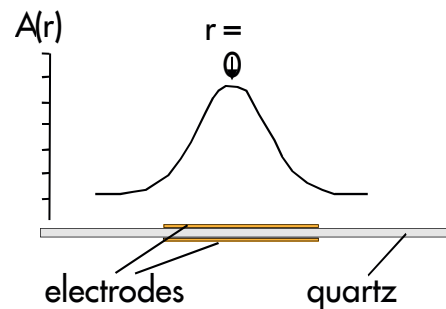


Figure A.5. A schematic illustration of how the amplitude of vibration, A, and the differential mass sensitivity, S, varies over the crystal.

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## The dissipation factor

The dissipation factor, D, is the inverse of the more known Q factor, defined by

$$D = \frac{1}{Q} = \frac{E_{dissipated}}{2\pi E_{stored}}$$

**(Equation 2.4)**

where $E_{dissipated}$ is the energy dissipated during one period of oscillation, and $E_{stored}$ is the energy stored in the oscillating system [1]. Consequently, D is the sum of all mechanisms that dissipate energy from the oscillating system such as friction and viscous losses.
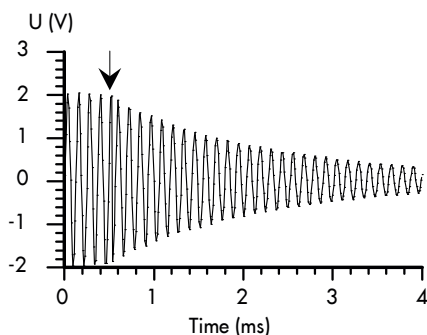


**Figure A.6. A typical decay curve.**

The dissipation factor of a quartz oscillator can be measured by recording how the oscillation decays after the oscillator has been excited into oscillation. In Figure A.6 a typical decay curve (curve that describes the decay of for example electric signals or acoustic waves). The arrow marks the time when the driving power was switched off [1].
Figure A.7 below shows a schematic illustration of how the decay curve is affected and changes its shape depending on the properties of the film on the crystal.
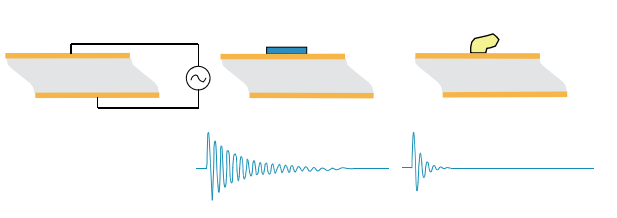


**Figure A.7. A schematic illustration of the AT-cut crystal at resonance and the decay curve with a rigid (middle panel) and a viscoelastic sample (right panel).**

## A3 References

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