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Quartz Crystal Microbalance a Powerful Technique for Nanogram Mass Sensing

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Abstract: A quartz crystal microbalance (QCM) is an acoustic transducer that sends an electronic signal when a mass change is detected on the sensor surface of an oscillating quartz-crystal resonator. QCM can detect a small amount of materials in the nanogram range quantitatively from the shift in resonance frequency under vacuum, gas phase, and a liquid environment. QCM is produced by oscillating a piezoelectric, single-crystal quartz plate to measure mass. Quartz's inherent property of piezoelectricity is the basis of QCM operation. This paper aims to review the role of quartz crystal microbalance in nanotechnology as mass sensing. One of the fundamental driving forces in nanotechnology that positively impact related research areas is new measurement techniques.

Keywords: QCM, Nanotechnology, Piezoelectricity, Resonance Frequency, Mass Sensing, Nanogram

1. Introduction

There are thirty-two classes of crystal, twenty of which have the piezoelectric effect. Quartz, or silicon dioxide (SiO_2), has proven to be the preferred material though several types of crystals have been used as frequency control elements. This is due to many physical, chemical, and electrical properties. Only quartz, for instance, yields crystal units that exhibit a zero frequency versus temperature characteristic (Buehler & Walker, 1949). Quartz crystal can be modeled as a circuit component using the commonly accepted "equivalent circuit". It is worth noting that a quartz crystal is a mechanically vibrating device, and that the equivalent circuit is an electrical model of a mechanical system (Lehmann & Bambauer, 1973). The electrical potential between the pressed surfaces in piezoelectric crystals is due to pressure

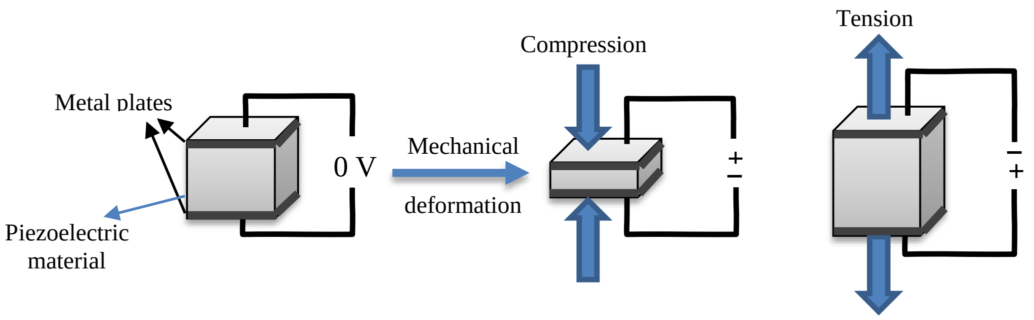

Figure 1: Piezo-electric effect when voltage is generated because of mechanical deformation

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on a small piece of quartz, and the voltage operation was caused by physical displacements (Curie & Curie, 1880). (Figure 1).

In 1959, QCM, which is still widely used in detecting mass-sensing, was introduced by a provider describing mass frequency relation for the foreign layers deposited on thickness-shear mode crystals (Sauerbrey, 1959). The mass increases when a film deposits on the crystal surface, and monolayer sensitivity is easily reached. However, viscoelastic effects will be observed and show their impact (Johannsmann, 2014). In the late 1980, it was found that if appropriate measures are considered to overwhelm the significances of the considerable moisture and viscoelastic properties, the QCM could be used in liquids that contribute vastly to the resonance properties (Kanazawa & Gordon, 1985). Nowadays, one of the numerous uses of the QCM measurement of viscosity is micro weighing (Figure 2).

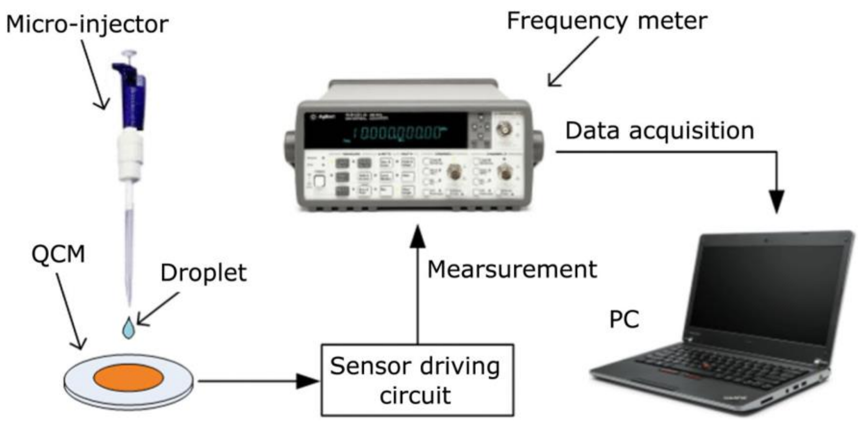

Figure 2: Schematic of measuring liquid properties with QCM (Tan et al., 2016).

The first piezoelectric mass-deposition sensor (QCM), the first biosensor and the first metal oxide semiconductor-based gas sensor were all developed in the 1960s (Rehman & Zeng, 2015). After that, however, the technology started to establish highly sophisticated devices that constantly grew toward increasing contraction and portable instrumentation starting from the 1970s and 1980s. In general, QCM is a mass detecting instrument that can detect mass variations similar to the formation of a monolayer (Kankare, 2002).

We are now blessed with the advancement of many important physical and chemical domains, as well as the ability to perceive the resulting mass changes. Of course, other physical and chemical changes may be used to explain similar events, but mass measurements are exciting because they are simple, direct, and absolute.

QCM is used by researchers increasingly in a scientific and technological field by controlling the environment required for many experiments. For example, in studying thin polymers, a quartz crystal microbalance is a valuable tool because of properties like; simple, cheap, practical, sensitive mass detector based upon the pressure electricity effect (Marx, 2003). The QCM has a significant progress explanation in measurement capability as a methodology; the method has a broad discovery range. For example, monolayer surface coverage can be decayed by small molecules or polymer films as an effect of the low mass while at the upper back, the larger masses bound to the surface can be sensed (Marx, 2003). These can be multilayered arrays of biomacromolecules and biopolymers. Another notable and unique characteristic of the technology is the ability to measure the mass and energy dissipation properties of films while conducting electrochemistry on solution species in real time. The methodology of electropolymerization of a film environment or state can be described by these measurements, containing the oxidation state for an active electro film driven by the underlying surface potential. The past decade has witnessed growth in applying the QCM technique to the study of widespread array of molecular systems at the solution-surface interface, particularly biopolymer and biochemical methods (Reviakine et al., 2011).

2. Construction of QCM

Piezoelectric is the heart of the QCM. Quartz stones are used to make wafers, which are used to make crystals for electronic applications. Nearly 90% of the crystals used in these applications are AT-cut. This implies that the stones are cut at a 35°15' angle to the Z-axis. The AT-cut was inserted among a couple of electrodes (Figure 3). Next, crystal blanks are cut at dissimilar orientations from quartz to accomplish definite required characteristics; the crystal structure determines the cut. The vacuum-deposited gold or silver films with a thickness of about 150 nm are the keyhole-shaped electrodes associated with the quartz resonator (Khanna, 2016).

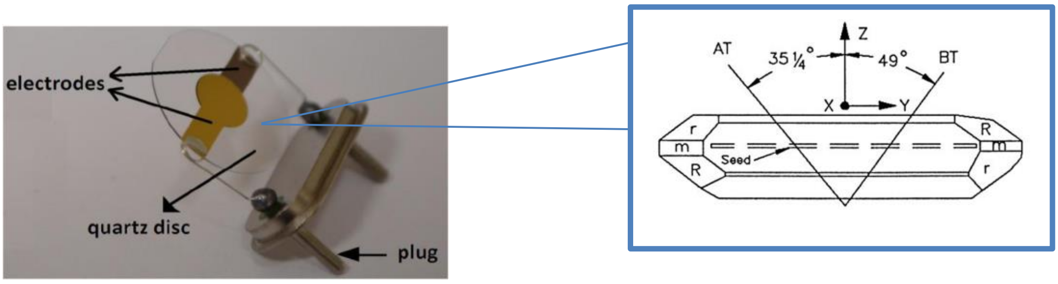

Figure 1: AT-cut QCM, upper and lower faces of the quartz possess Au electrodes (Barzinjy et al., 2017)

2.1 How does QCM work?

The piezoelectric effect of a thin quartz crystal made up of two electrodes used in QCM (Figure 4). The piezoelectric effect is the electrical potential generation of the material due to mechanical stress is applied, and the vice versa process is possible, i.e., a deformation. Thus, the quartz crystal starts to oscillate when an alternating electric field is applied to the electrodes in QCM. A transverse acoustic wave begins accordingly to the vibration motion of the quartz crystal that travels across the crystal and reflects into the crystal at the surface. When the joint thickness of the crystal and electrodes is equivalent to the acoustic wavelength, a standing wave condition is established. Therefore, the system's resonance is very sensitive to the crystal/electrode system's consistency and acoustic frequency (Khanna, 2016).

Therefore, the fundamental frequency of the QCM will decline with increasing mass placed on the crystal, as there is a consequential increase in the thickness of the piezo-electrode system (Roy et al., 2010). The consequent change in frequency can be analytically connected to the change in the group (per unit area) at the crystal surface induced by absorption or deposition of a substance (using the

Sauerbrey equation). This permits an exact derivation of microscopic mass dynamics per unit area. In using functionalized crystal surfaces, definite molecules can be targeted either for chromatographic analysis or to monitor a given interaction of interest (Ferreira et al., 2009).

The frequency of the QCM is also alerted to increasing viscosity of liquid media around the plate and increasing roughness of the electrodes; thus, functional designs tuned to these factors can be implemented by a QCM if wanted. Alongside the frequency measuring the changes to the dissipation of the QCM crystal is also possible, which measures the damping of the crystal energy affected by a sample and can be used to infer material properties (visco-elastic nature) (Barzinjy & Zankana, 2016).

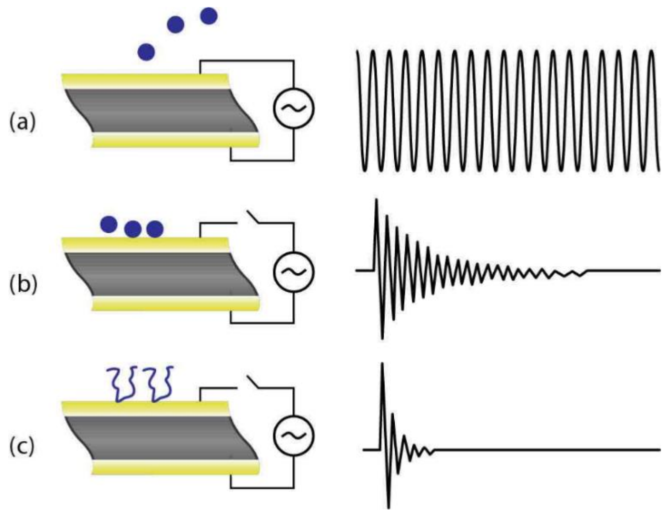

Figure 4: Schematic representation of the principle of QCM-D. (a) The oscillation frequency decreases as mass adsorbs on the surface. (b) Rigid mass couples well with the crystal, leading to a long decay curve. (c) Viscoelastic mass couples poorly with the crystal, leading to a short decay curve. (Illustration copyright belongs to Biolin Scientific/Q-Sense. Reproduced with permission from Barzinjy et al., 2017)

3. Nanotechnology and Nanogram Sensing

In the second half of this decade, we are witnessing the emergence of a new frontier in science. Researchers are pushing the boundaries of nanotechnology's medical applications. The discovery and innovations of a class of peculiar hollow carbon molecular aggregations known as fullerenes sparked interest in this field of study in the 1980s (Abraham et al., 2008). These technologies include nanoparticles (NPs), nanoarrays, nanopore technology, protein arrays as an apparatus in nano sensors and immunoassays. Even though new materials become available as more molecular entities are discovered as amenable to nanoscale design and fabrication, gold NPs and quantum dots (semiconductors) are the most widely used. Crystal materials are unique in properties and are mostly chosen for their durability and piezoelectric properties of developing and retaining an electric potential (charge) when subjected to mechanical stress. Materials like gallium, phosphate, quartz, and ceramic are the primary examples of this family. Nano biosensors are another area of development in which antibody-based piezoelectric nano biosensors are well technologically advanced (Jain, 2005).

4. Mass Sensitivity of QCM: Sauerbrey's Equation

The quartz crystal microbalance contains a thin vibrating quartz wafer sandwiched between two metal excitation electrodes. Using the mass dependence of the QCM resonant frequency, QCM has been used to determine interfacial mass changes. Due to the high sensitivity of QCM's sensor, it has been extensively studied in a variety of domains over the last few decades, including chemistry, physics, and biological fields (Zhang et al., 2015). Describing the mass-frequency relationship at the QCM surface, Sauerbrey put forward the famous Sauerbrey equation:

$$\Delta m = -C_{QCM}\,\Delta f \qquad [1]$$

where Δm is the mass change and Δf is the frequency shift, respectively. C_{QCM} is 17.7 $ng \cdot cm^{-2} \cdot Hz^{-1}$ for 5 MHz AT mass sensitivity constant.

Sauerbrey, through his equation, stated a theoretical basis for using QCM to measure the gas phase. The QCM has been frequently used to detect a variety of nanoscale target analytes in liquid and gas environments based on the Sauerbrey equation and other models (Kanazawa and Cho, 2009) due to advantages including good selectivity of the surface, simplicity in operating, etc. (Marx, 2003).

It must be noted that the sensitivity of the mass in the detection area of 1 square centimeter is about 5.65×1010 Hz/kg (the reciprocal of CQCM). Therefore, due to the influence of the energy trap in the quartz crystal resonator, the mass sensitivity of the QCM is distributed as a Gaussian curve in the radial direction instead of having similar mass sensitivity on the entire surface. Both theory and experiment show that the mass sensitivity distribution of QCM coated with "mm" electrodes is close to the Gaussian curve (Josse et al., 1998). In addition, to ensure the regular oscillation of QCMs, it is necessary to plate a layer of metal electrodes on both sides of the quartz wafer. The mass sensitivity function of QCM may vary depending on the material, shape, thickness, and size of the metal electrode (Josse et al., 1998).

In particular, the mass sensitivity constant CQCM in the Sauerbrey equation is only related to the material constant of the quartz crystal, and the Gaussian distribution characteristics of the mass sensitivity and the influence of the electrode metal are not considered at the same time. Therefore, using the unconstrained Sauerbrey equation to calculate the mass change on the QCM surface may cause errors (Figure 5).

Lastly, three conditions make Sauerbrey's equation valid: (i) in comparison to the crystal group, the loaded mass should be small. (ii) The packed mass should be strictly adsorbed, and (iii) there is an active area on the crystal's surface, which the group regularly can be distributed over it (Vogt et al., 2004).

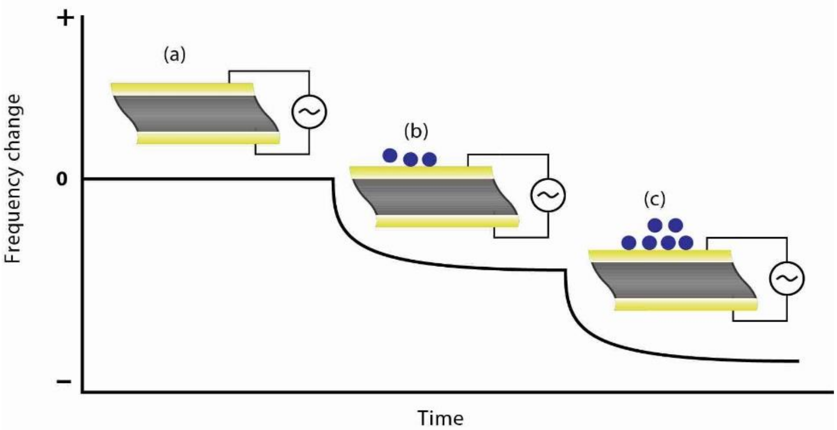

Figure 5: A schematic depiction of Sauerbrey's findings (a) at the beginning of the operation, (b) less mass attached to the QCM, and (c) more mass attached to the QCM

5. The Applications of QCM

The sensitiveness of the technique in liquid at maximum is less than one ng/cm^2. The eventually measured thickness of the film can differ depending on the rigidity of the film from hundred nanometers to a few microns. There are extensive ranges of applications in several fields of science for QCM. Examples include molecular interaction dynamics (such as protein interactions), molecular surface interactions (such as the affinity of biomolecules for functionalized surface binding sites), the accumulation of polymer membranes and their interactions with different components of liquid media, various surfactants in various coatings, biosensor applications, etc. (Cheng et al., 2012). However, the determination of the adsorption properties of biomaterials is the main application of QCM (Figure 6), Bioanalytical and functional surfaces for proteins lipids, polymers, cells, and bacteria as exemplified in the following figure (Nilebäck et al., 2011).

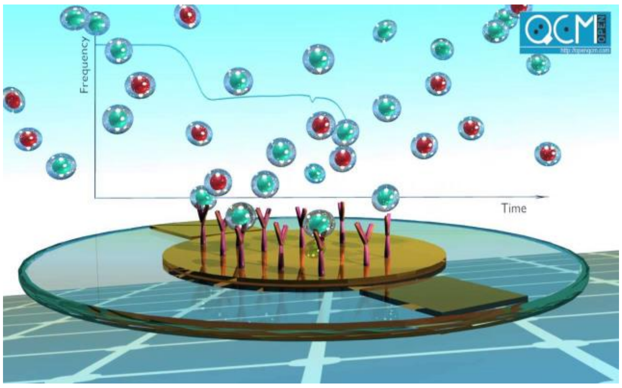

Figure 6: Affinity of bio-molecules to the binding site of a functionalized surface

QCM and vacuum deposition systems are entering the field of chemical analysis. These instruments were almost exclusively used to measure the thickness of thin films in vacuum systems (Ward & Buttry, 1990). Most manufacturers of vacuum deposition systems sell QCM equipment as accessories. However, as technology advances, people realize that they can benefit from the use of liquids. Therefore, when QCM for liquids is improved, applications, including electrochemistry, are improved.

The piezoelectric effect in QCM causes the sound wave to propagate through the glass when an oscillating electric field is applied through the device and to reach a minimum impedance when the device thickness is a multiple of the half-wavelength of the sound wave. Acoustic waves propagate perpendicular to the crystal surface in QCM, which is why it is called a shear mode device. Although QCM is now widely known, its amount of information is not particularly large, and sometimes it is not accurate. Several other types of quartz devices can be used as microbalances. However, the general response of quartz crystal microbalances is double-edged, which expands and limits the application. QCM is not like a microbalance at all, but responds to characteristics such as viscosity. Therefore, the thickness slice mode resonator is a more accurate definition of the device. This description conveys information about the properties of sound waves, like surface acoustic waves, bending plate waves, and other acoustic modes (Ferreira et al., 2009). The frequency of the acoustic wave is determined by the mass deposited on the device (active region) or the complete device (glass plus electrode), and it varies with the device's effective mass. As a result, the thin-film group adhering to the crystal surface can be determined using the device's resonant frequency change. As the name suggests, QCM can measure minute materials, and the smallest detectable mass change is usually ~ 1 ng / cm^2. For many years, QCM was just a quality detector; the challenge was to adjust the surface chemistry so that the device could be a discriminating quality detector (Gizeli et al., 2003).

For the gas phase or liquid phase, QCM, all you have is a circuit to drive it and some frequency counting equipment. You may have a small piece of hardware that can convert the frequency output to a number that is meaningful for your specific application (Voinova et al., 2002). There is a wide range of applications of quartz crystal microbalances. QCM can be utilized in thin film deposition process (Elam et al., 2002), viscosity and surface tension measurement (Lin and Ward, 1996), stress/strain application (Johannsmann et al., 2021), simultaneous measurement of mass and temperature devises (Santos et al., 2011), analytical chemistry (Daikhin et al., 2002), protein identifying (Liu et al., 2008) and space system contamination studies (Dirri et al., 2019).

The simplicity of the device means that it is relatively inexpensive. The characteristic of these QCM devices is their low manufacturing cost. QCM technology is widely used in liquid biochemical applications. However, the main challenge remains to improve the sensitivity, detection limit, and the ability and reliability of multiplex analysis (Michalzik et al., 2005).

6. Conclusion

This review outlined the background principles of QCM and highlighted recent applications regarding nanogram mass sensing. The review showed that the technology has reached a point where commercially available instruments exist and associated theoretical models required for interpreting data in meaningful physical parameters such as mass, thickness, density, viscosity. In addition, the current developed in QCM can make mass measurements on the order of nanograms with only a 1% margin of error, potentially enabling the weighing of individual molecules in liquid environments. These achievements, plus the various publications using the instrument, of which only a tiny number are described in this text, help lay the groundwork for the QCM-D technology transitioning into a standardized approach for addressing questions about biological materials and their interactions.

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