Design for Biosecurity

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Lecture 13

Principle of Quartz Crystal Microbalance (QCM)

Welcome back! We are now in the third week of our course, and as I mentioned in the previous class, today we will be discussing the Quartz Crystal Microbalance (QCM) in more detail. But before diving deeply into its principles, let me refresh your memory with a concept you might be familiar with, piezoelectricity. Many of you probably encountered this concept during your studies in the 11th or 12th grade.

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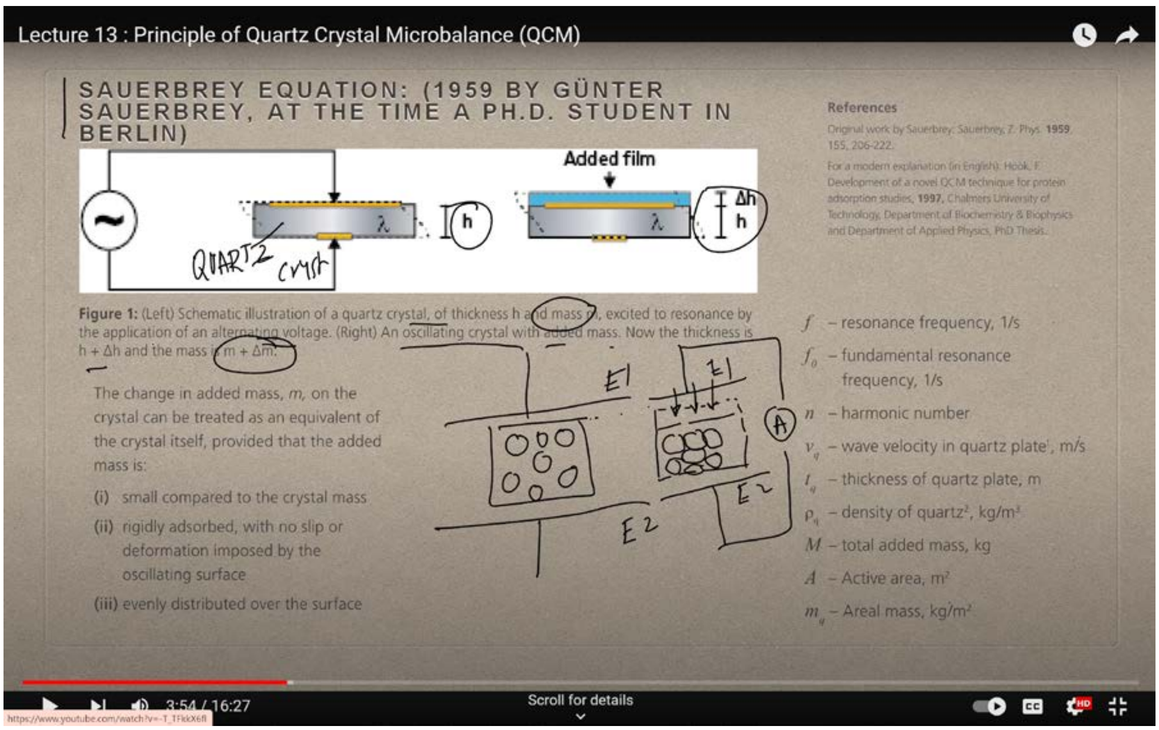

Piezoelectric materials are special materials that generate electricity when subjected to mechanical stress, such as compression or pressure. Essentially, when you apply a force to these materials, they produce an electrical output in the form of current or voltage.

Now, let's break that down a bit more. What actually happens when a material displays piezoelectric behavior? Imagine we have a material, and within it, the atoms are naturally spaced out in a certain configuration. If we place two electrodes on either side of the material, labeled as E1 and E2, and apply compression, the atoms within the material will begin to shift closer together. This change in atomic spacing causes a corresponding shift in the electrical properties between E1 and E2, leading to a measurable change in voltage or current across the material.

These materials, which exhibit this piezoelectric behavior, are known as piezoelectric materials. A Quartz Crystal Microbalance (QCM) is one such device that utilizes piezoelectric materials for sensing purposes.

Now, let’s delve into more specifics regarding the Quartz Crystal Microbalance. One of the foundational figures in this field is Gunther Sauerbrey, who, in 1959 during his PhD research, introduced the key principles of QCM. His work established the Sauerbrey equation, which is essential for understanding QCM.

Imagine a quartz crystal with two electrodes placed across it. The crystal has a certain thickness, denoted as "H," and a mass, "M." When you apply an alternating voltage across the crystal, it begins to oscillate at a specific resonance frequency. Now, suppose we add additional mass to the crystal, this changes both its thickness (now $H + \Delta H$) and its mass (now $M + \Delta M$).

So, what does this mean in practice? Take a quartz crystal, for instance. If we add a mass to the surface of the crystal, it affects the oscillation of the crystal. This change in oscillation due to the added mass is the core of how QCM functions as a highly sensitive sensor for mass detection.

What you’re seeing in the slide illustrates exactly what I’m explaining. When a mass is added to the quartz crystal, as shown in the diagram, the mass will compress the material. In this situation, two possible outcomes can occur: the crystal may generate a current, or alternatively, I could apply a current and observe some change. It’s a reciprocal process.

Now, when we refer to the Sauerbrey equation, it forms the foundation of the Quartz Crystal Microbalance (QCM). There are certain key parameters to consider, which I will revisit shortly. These include the resonance frequency, fundamental resonance frequency, harmonic number, wave velocity in the quartz plate, thickness of the quartz plate, total added mass, active area, and active mass. These concepts will all come together as we explore this in more depth.

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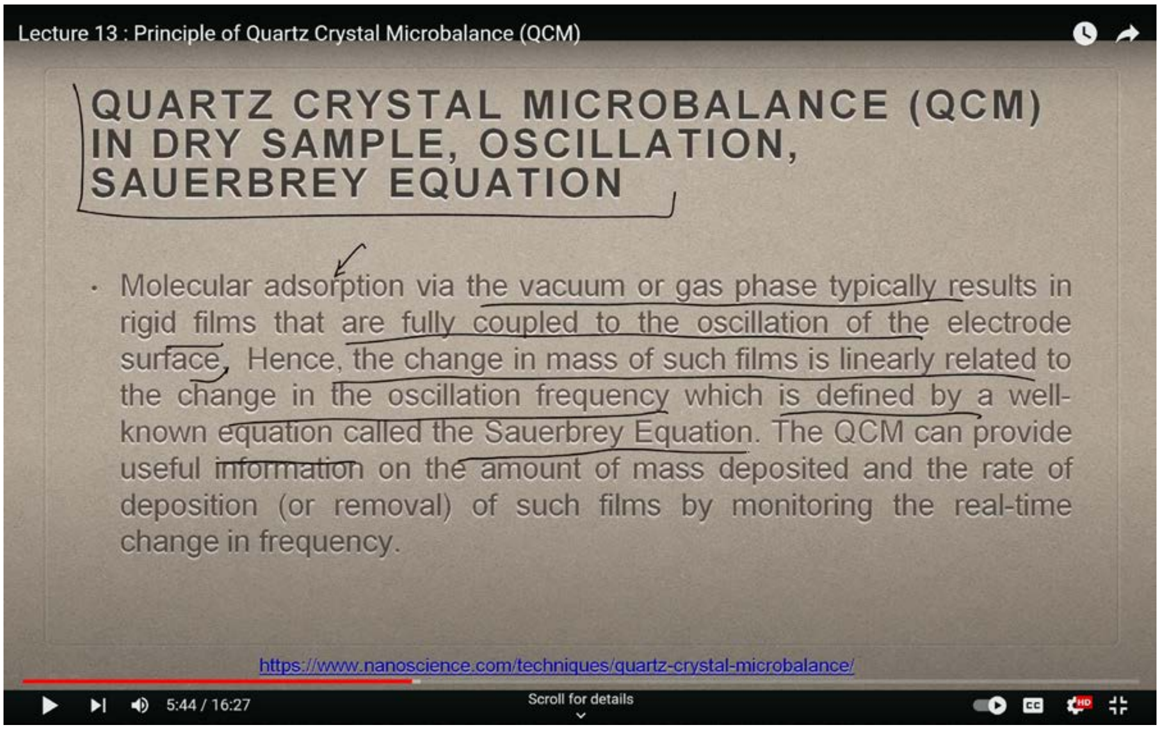

Before I get into the specifics of the slide, let’s discuss how the QCM operates with a dry sample, the oscillation process, and how the Sauerbrey equation fits into this. In typical scenarios, molecular adsorption via vacuum or gas phase leads to the formation of a rigid film that is fully coupled to the oscillation of the electrode surface. As a result, any change in the mass of this film is directly proportional to the change in oscillation frequency, as predicted by the well-known Sauerbrey equation.

What does this mean? Let’s imagine we have a quartz crystal oscillating at its natural frequency. If we add a mass to it, what happens? The crystal, initially vibrating at its natural frequency, will experience a decrease in that frequency as the mass increases. This decrease in frequency is directly related to the added mass. In essence, the change in mass is linearly related to the change in oscillation frequency.

The QCM is a valuable tool because it provides real-time insights into the amount of mass being deposited or removed. By monitoring changes in frequency, we can determine the amount of mass added or removed and the rate of these changes. This entire process is governed by the principles of piezoelectric resonance.

To give you more context, the operation of QCM is based on the piezoelectric effect, which occurs in specific crystalline materials, those that have a certain type of crystallography, known as non-centrosymmetric materials. Quartz is one such crystal, and the term "piezoelectricity" originates from the Greek word "piezo," meaning "to press." Piezoelectricity refers to the electricity generated in response to applied pressure in these materials.

Let’s take a step back to this slide. When you apply pressure, whether through adding mass or by another means, the frequency of the crystal changes. Depending on the mass you add, the frequency will either increase or decrease, but it will definitely change. Piezoelectricity is therefore defined as the generation of electricity in response to mechanical deformation caused by mechanical stress. Conversely, it also refers to the physical deformation of a crystal in response to an applied electrical field.

The piezoelectric effect was first discovered by French physicists Pierre and Jacques Curie in 1880, when they demonstrated that certain salt crystals could generate electricity when deformed along specific crystallographic orientations. The following year, they further demonstrated the converse effect: applying voltage to a crystal could cause it to deform.

This is exactly what I was trying to explain in the first slide. For instance, if you compress the material, you’re applying physical pressure, this is a case of compression. But now imagine instead of compressing it, you apply a voltage across the material. Picture this: these two wires, represented by my fingers, are connected to the material. When you apply voltage across it, the material will undergo compression and experience structural changes. It's a reversible process.

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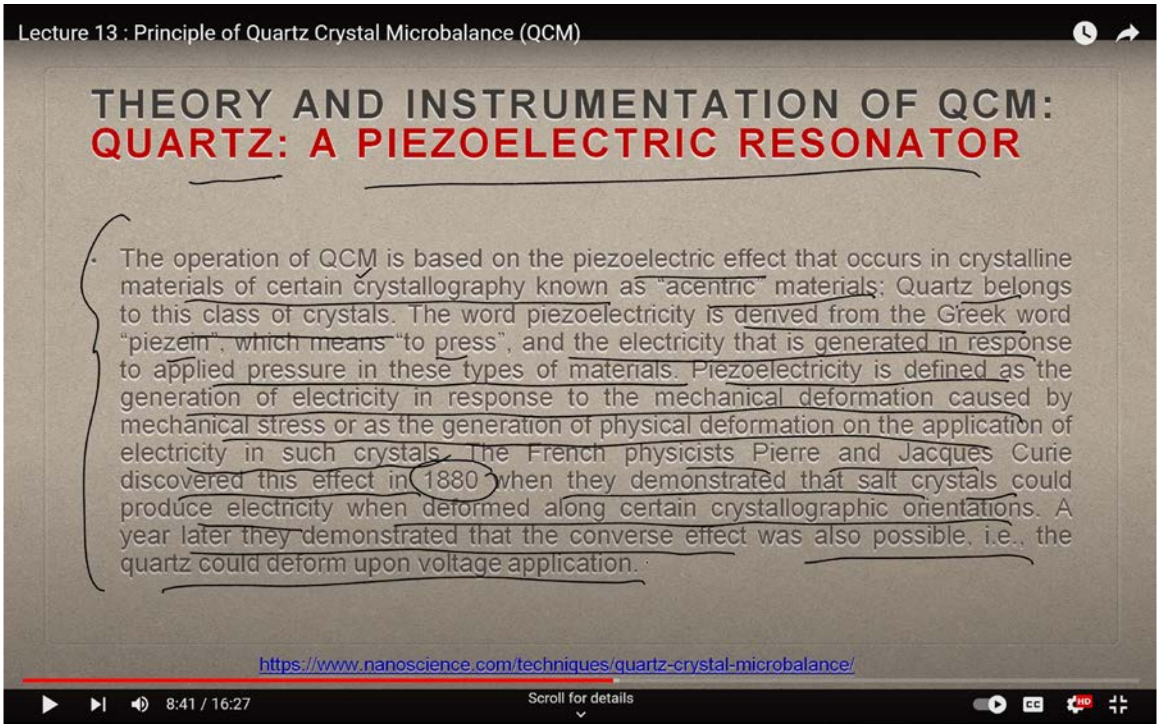

You can generate electricity by physically compressing the material, or you can apply electricity to induce compression. This principle is what makes piezoelectric materials so fascinating. When you compress the material, as shown in the earlier illustration, the molecules start off in one arrangement, and after compression, they shift closer together, generating electricity. But this can also happen in reverse. By applying a current, you can force the material into the same compressed state, deforming the structure.

This is the unique characteristic of piezoelectric materials, and this is why the Quartz Crystal Microbalance (QCM) has become such an important tool for measuring mass in terms of frequency shifts. It all began with Gunther Sauerbrey's PhD thesis in 1959. He developed the fundamental principle on which QCM operates, and since then, the technique has evolved based on that original concept.

To revisit the core idea: the operation of the QCM is rooted in the piezoelectric effect that occurs in specific crystalline materials, known as acentric materials. The term “piezo” means “to press,” and the electricity generated in response to applied pressure within these materials forms the foundation of QCM technology.

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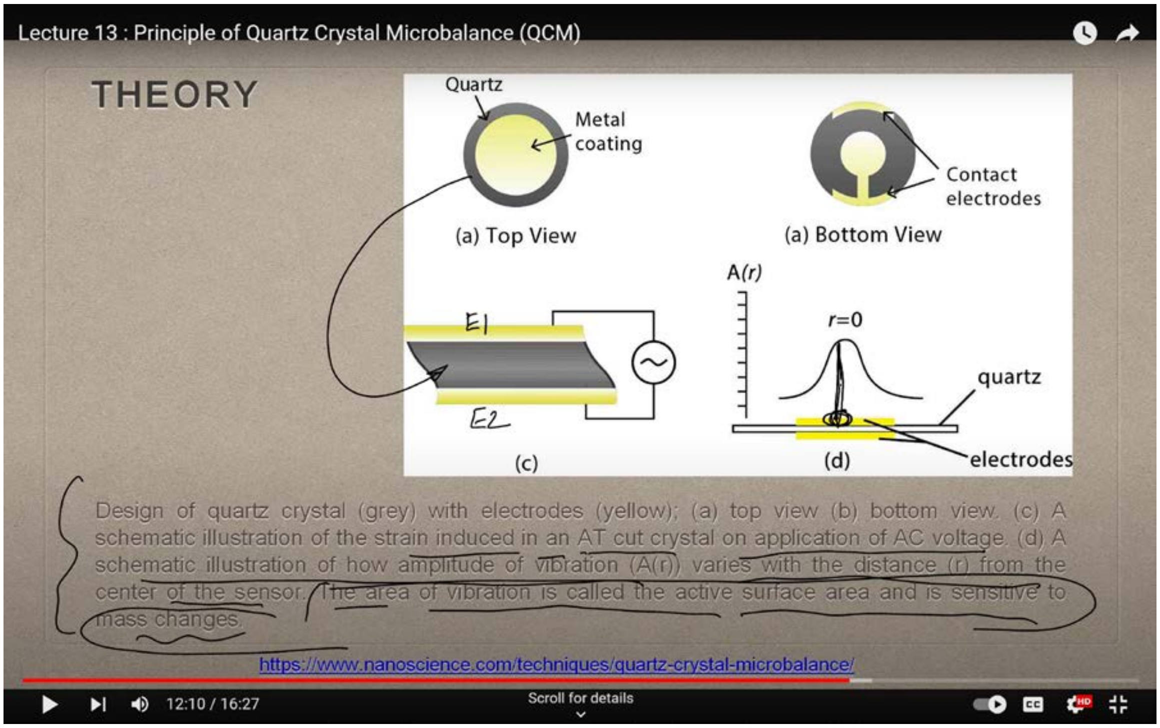

Once you understand this, let’s dive deeper into the theory and mechanics. Here’s an illustration to clarify. You have a quartz crystal with a metal coating, and this crystal is sandwiched between two electrodes, let’s call them E1 and E2 for reference. The design of the quartz crystal with these electrodes allows us to observe how strain is induced when an alternating current (AC) voltage is applied. The illustration shows how the vibration amplitude varies with distance from the center of the sensor. This vibration area is known as the active surface area, and it is highly sensitive to changes in mass.

The central area of the crystal is where the sensitivity is highest. The central sensitivity tapers off as you move toward the edges of the crystal. At the peak of this central node, you observe maximum sensitivity, and this decreases gradually toward the corners where the sensitivity is much lower. The active surface, which corresponds to this central peak, is critical when considering mass sensitivity in QCM.

Now, let’s discuss the relationship between mass sensitivity and the Sauerbrey equation. The frequency change in a QCM can be measured with extremely high precision, down to a resolution of one hertz or even lower. This is particularly true for crystals with fundamental resonance frequencies in the megahertz range. Quartz crystals are highly stable as resonators, which is why they’ve been used in electronic filters, frequency control devices, and ultrasonic transducers since the early 1900s.

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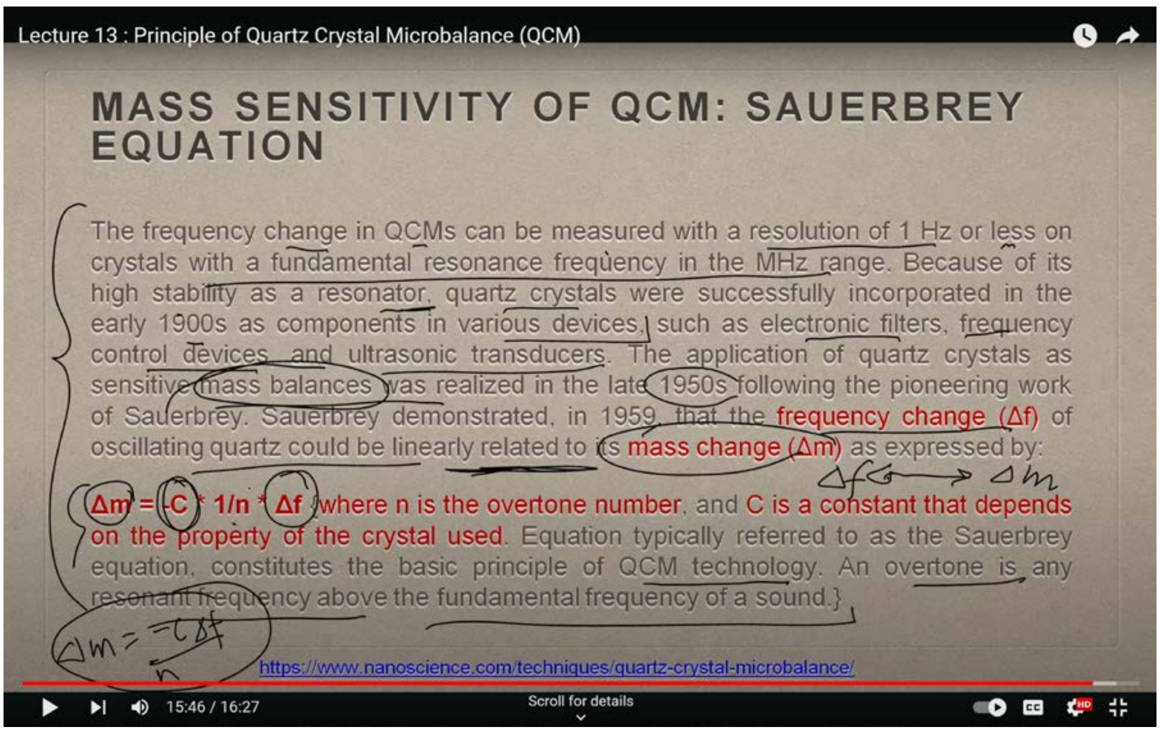

However, it wasn’t until the late 1950s that the quartz crystal was recognized for its potential as a highly sensitive mass balance. Following Sauerbrey’s groundbreaking work in 1959, he demonstrated that the change in frequency (Δf) of a quartz crystal is directly proportional to the change in mass (Δm). This linear relationship, described by the Sauerbrey equation, remains the cornerstone of how QCM technology functions today.

So, there is a clear relationship between the change in mass (Δm) and the change in frequency (Δf) in Quartz Crystal Microbalance (QCM). The equation, which I'm presenting here without diving into the full derivation, is as follows: Δm is equal to a constant, typically denoted as C, multiplied by Δf, all divided by the overtone number n. Formally, this is written as:

$$\Delta m = -\frac{\mathrm{C}^* \, \Delta f}{\mathrm{n}}$$

This equation, often referred to as the Sauerbrey equation, forms the fundamental basis of QCM technology. It describes how the frequency shift is related to the added mass on the quartz crystal.

Now, when we talk about overtones, we are referring to any resonant frequency that is above the fundamental frequency of a material or system. Every material has a fundamental frequency, which is its base frequency of oscillation. Anything above this base frequency is referred to as an overtone, which can be expressed as overtone numbers n. These higher harmonics play a significant role in understanding the behavior of oscillating systems, whether in QCM or acoustics.

Speaking of overtones, you may find it fascinating to explore something called overtone singing. This is a unique form of vocal expression that produces resonant frequencies above the fundamental tone. If you're curious, I highly recommend checking out some incredible overtone singing performances on YouTube. For example, in regions like Tibet and the Himalayas, particularly in places like Himachal Pradesh, overtone singing is a traditional form of chanting or prayer. The distinctive humming sound you hear in this style of singing is produced by generating multiple harmonics above the base voice frequency.

By watching these videos, you'll gain a deeper understanding of overtones and how they influence voice modulation, which will help you grasp the concept of overtone numbers n in the context of QCM and beyond. Thank you.