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Calibration Of The Quartz Crystal Microbalance For LB Films Measurement

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Abstract

The Quartz Crystal Microbalance (QCM) can measure extremely small quantities of mass using the linear relation between mass change on the electrode and resonance frequency change of a quartz crystal resonator. An electrode of a quartz crystal resonator sensing the mass of the deposited materials has a distribution of mass sensitivity which varies with the location. And the vibration is not restricted within the electrode of the quartz crystal resonator composed of the planar crystal less than that of plano-convex or biconvex crystal used in vacuum-evaporated film thickness-monitor. The frequency constant used to calculate the mass of material deposited over the entire surface of the electrode(N_1) does not accord with that in Sauerbrey's equation(N) which describes a relation between the mass of material deposited on the electrode and the resonance frequency change of a quartz crystal resonator. We obtained the frequency constant(N_1) and the distribution curve by vacuum-evaporation of thin gold film of known weight on a quartz crystal resonator in preparation for investigating the behavior of LB films (Langmuir-Blodgett films) in air and in water.

1. INTRODUCTION

The QCM has been used for measuring thicknesses of vacuum-evaporated films[1], quantities of gas adsorption[2], aerosol mass concentration[3)-6], and so on, because it can weigh materials as light as five or six nanograms. Evaporation rates of water from LB films into air, the flaking quantity of LB films from substrates, and swelling behavior of LB films by absorbed water[7)-9] have also been studied using the QCM.

Each quartz crystal resonator has its own resonance frequency f_0(Hz), which depends on the crystal plane by which a quartz crystal is cut. When material whose mass m(g) is to be determined is deposited on the electrode of the quartz crystal resonator, the resonance frequency changes to $f_0+\Delta f$(Hz). Deposited mass m(g) and frequency change Δf(Hz) have three relations, one of which is called Sauerbrey's equation[10], and is expressed applied in the air, as:

$$\mathrm{m}=\frac{\mathrm{d}\times\mathrm{N}\times\mathrm{A}}{\mathrm{F_0}^2}\times\Delta f \cdots\cdots(1)$$

where d(g/cm^3) is the density of the quartz crystal being used, N(cm•Hz) is the fre-

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quency constant for the AT-cut quartz crystal (1.67×10^5 cm•Hz) and A(cm^2) is the area of the electrode of the quartz crystal resonator. This equation is limited that Δf is within 2% of f_0[11]. Remaining two equations are supposed out of linearity between Δf and m. One is called "Period-measurement Technique", indicated with $\tau_0=1/\mathrm{f}_0$ and $\tau=1/(f_0+\Delta f)$ as,

$$\mathrm{m}=\mathrm{d}\times\mathrm{N}\times\mathrm{A}\times(\tau-\tau_0)=-\frac{\Delta f}{\mathrm{f}_0(\mathrm{f}_0+\Delta f)} \quad\cdots\cdots(2)$$

This equation can be applied in the range of 10% of f_0[11),12]. The other is "Miller and Bolef's equation" and shown as,

$$\tan\frac{\pi(\mathrm{f}_0+\Delta f)}{\mathrm{f}_0}=-\frac{\rho_\mathrm{f}\mathrm{V}_\mathrm{f}}{\rho_\mathrm{q}\mathrm{V}_\mathrm{q}}\tan\frac{\pi(\mathrm{f}_0+\Delta f)}{\mathrm{f}_\mathrm{f}} \quad\cdots\cdots(3)$$

where $\rho_\mathrm{f}\mathrm{v}_f/\rho_\mathrm{q}\mathrm{v}_q$ is the ratio between the shear-mode acoustic impedance of the deposited material and that of the quartz, f_f is mechanical resonance frequency of the deposited film determined[13]. This is consistent within 15% of f_0[11] and used for vacuum-evaporation thickness monitor these days. There are three equations which relate the resonance frequency change to the mass of deposited film, however, Sauerbrey's equation is enough in the extent of our use.

Quartz crystal vibrates in thickness-shear mode, mass sensitivity decreases with the distance from the center of electrode proportional to exponential curve. Analysis of the vibration in the quartz crystal has been investigated elsewhere[14)-18], most of them were not the mass sensitivity distribution, which were determined using the electrical polarization, the speckle effect and so on. So were a few of them, however, they were investigated to make much mass which is a few percents of mass of crystal plate deposited on the electrode. While LB films deposition, it is useful to study for dynamics of LB films and water molecules in LB films to obtain mass sensitivity distribution curve in the order of some hundred nanograms. As described above the QCM has been used for various measurements, however, different from vacuum-evaporation thickness monitor, LB films are deposited all over the quartz crystal resonator, namely the quartz crystal plate and the electrode. We have to take into account of the vibration outside the electrode, stray electric field. In this paper, considering the use of the QCM in air or in water as a microbalance of LB films, we obtain the mass distribution curve, that is, a distribution of mass sensitivity from location to location, investigate the effective frequency constant, and investigate the precision of the quartz crystal resonator as a microbalance.

2. EXPERIMENTAL DETAILS

The QCM shown in Fig. 1 is composed of four parts: (1) two quartz crystal resonators, one of which senses mass and the other which is a reference resonator. Both of these resonators are AT-cut crystals and stable under temperature change[19] (temperature coefficient $\Delta f/f=0$ at 25℃, $|\Delta f/f|\leqq0.76\times10^{-7}$ between 25±1℃), (2) an oscillating circuit containing three TTLs driven at 5V d.c. dry battery[20], (3) a frequency counter (IWATSU UNIVERSAL COUNTER; SC-7202) and (4) a personal computer (IBM; PS/55) which indicates graphically the mass change on the electrode at one-second intervals. The QCM works at about 22℃ and in a clean room for stabil-

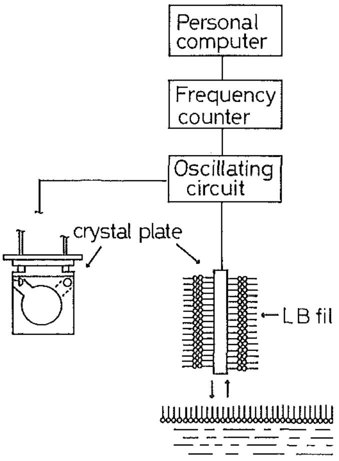

Fig. 1 Schematic diagram of Quartz Crystal Microbalance (QCM)

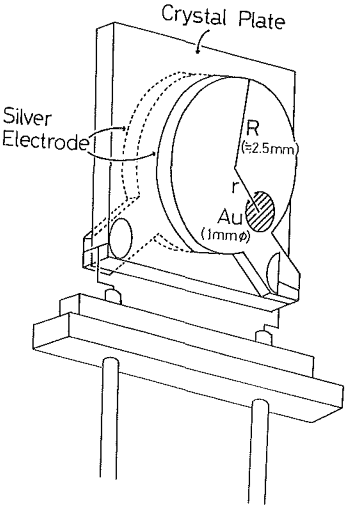

Fig. 2 Quartz crystal resonator

izing quartz crystal resonance. The quartz crystal resonator, (9MHz, HC-18/U ; YA-KUMO TSUSHIN, TOKYO) on which silver is evaporated as an electrode is shown in Fig. 2.

In the vacuum evaporation process, three quartz crystal resonators are set up on the sample holder made of brass, and evaporated simultaneously at equal distances from the evaporate source of gold. For obtaining the mass sensitivity distribution of the electrode, the thin gold film, whose radius is 0.5(mm) is vacuum-evaporated on the silver electrode using polyester masks. The radius of each electrode R(mm) is about 2.5(mm). The distance of the thin gold film from the center of the electrode as measured by an optical microscope with a scale counter is r(mm).

3. RESULTS AND DISCUSSION

3. 1 Measurement of the deposited mass over the entire surface of the quartz crystal plate

First, gold is deposited over the entire surface of the quartz crystal plate. The mass of the evaporated thin gold film is defined in two ways, termed m_0 and m_1 • m_0 is defined as follows,

$$\mathrm{m_0} = \text{(evaporated mass of the gold from the source)} \times \frac{\text{(solid angle of the evaporated gold thin film)}}{\text{(solid angle of the sphere : } 4\pi\text{)}} \cdots\cdots (4)$$

m_1 is calculated from the change of the resonance frequency of the QCM(Δf) according to equation (1).

The value of m_1/m_0 is 0.73 as a consequence of the evaporation over the entire surface of the crystal plate. When a mass deposited over the whole surface of the crystal plate is measured by the QCM, we need to multiply m_1 by 1.37 (=1/0.73). Sauerbrey's equation (1) is derived from a differential equation based on Newton's equation of motion and Hooke's law under certain conditions, namely, that the quartz crystal plate is very thin compared with the length and width of it and all ends are free[21]. Calculating the values under the above conditions reveals the frequency constant $N=1.67\times10^5$(cm•Hz). From the above results, if the difference between m_1 and m_0 corresponds to that of the frequency constant only, the effective frequency constant in this case is $N_1=2.29\times10^5$ (cm•Hz). The frequency change 1(Hz) corresponds to 1.88 (ng) on the electrode of the quartz crystal resonator.

Next, gold is deposited over the electrode only. In this case the value of m_1/m_0 is 0.75. The difference between the cases of the covering of the entire crystal plate and the electrode only shows that a small greater area than that of the silver electrode can sense a mass, because a little outer area of the electrode vibrates with a stray electric field from the electrode edge. Comparing 0.73 with 0.75, it is found that the electric field exists in 1.03 times as great area as that of the electrode; the shell width of the stray field is 0.34 (mm).

3.2 Measurement masses of the any shape at any location on the electrode

A few experiments were performed to consider the measurement masses of random shapes at any location on the electrode The relation between m_1/m_0 and r/R, that is, the mass sensitivity distribution, is shown in Fig. 3. In this case, the diameter of the deposited thin gold film is 1(mm). It is found that the central area of the electrode is more sensitive than the circumference. The measured points greater than 1 of r/R correspond to the interconnecting area of silver electrode with the output lead. The solid line was obtained from the measured values by the least squares method. The broken line is the theoretical line calculated using Energy-Trapping Theory[18,22,23]. In calculation, the thickness of the silver electrode of the quartz crystal resonator is used and measured about 800～2000 Å by the Stylus Instruments. We utilize 1100 Å as the average value, because we can find little difference between the mass sensitivity distribution curves. Theoretical curve greater than 1 of r/R indicates the vibration at the crystal outside the electrode. From this, the vibration occurs until 10% outside of

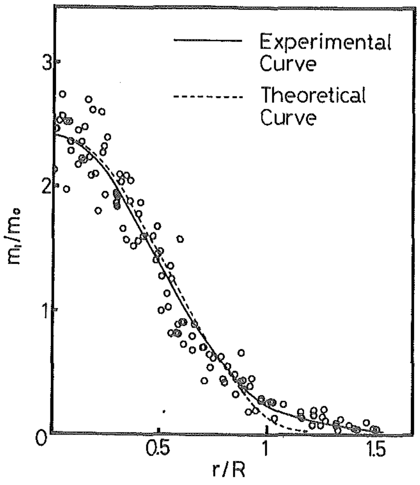

Fig. 3 Location dependence of mass sensitivity distribution

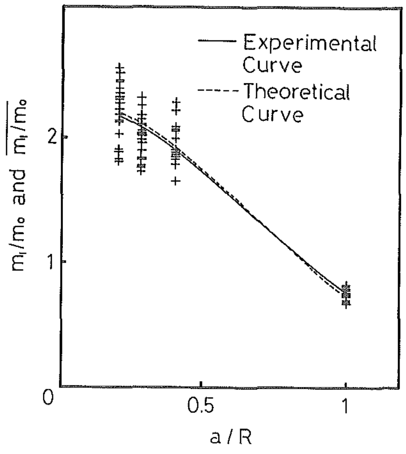

Fig. 4 Radius dependence of mass sensitivity distribution

the electrode to radius direction by a stray electric field from the edge of the electrodes. This result corresponds well withthe result of the chapter 3-1.

Gold is deposited at the center of the electrode with the radius a of 0.5, 0.7, 1.0 and 2.5(mm). In Fig. 4 the measured values (the cross points) obtained by using equation (2) for m_0 and the change of the resonance frequency of the QCM for m_1, and a average curve (the solid line), obtained from the mass sensitivity distribution of Fig. 3 with $N=1.67\times10^5$ (cm•Hz), are shown. The average curve is obtained by calculating the mean value $\overline{m_1/m_0}$ of m_1/m_0 in Fig. 3 changing the value a/R by

$$\overline{m_1/m_0} = \int_0^{a/R} (m_1/m_0) d(r/R)/\pi(a/R)^2 \quad \cdots\cdots\cdots (5)$$

The broken curve is calculated using Energy-Trapping Theory. It is found that the value $\overline{m_1/m_0}$ corresponding smaller radius a is higher than the larger one. The measured values are slightly different from the theoretical curve. It is found from the figure that the error of the mass values obtained from the QCM mentioned above is 20% at most. We will be able to estimate the mass of materials of any shape deposited at any location on the electrode using the above mass sensitivity distribution curve.

4. CONCLUSION

We has found that mass sensitivity distribution curve was obtained not being affected by the finite dimensions of the gold evaporated films. The electric field exists in an area 1.03 times as great as that of the electrode, which shows good agreement with the theoretical value of Energy-Trapping Theory. When LB films are deposited, it is necessary to take it into account and obtain a real value of mass by multiplying the mass calculated from the QCM by 1.33.

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