In-Situ and Ex-Situ Monitoring of Electrochemical Deposition of Silver Using Quartz Crystal Resonators

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Electrochemical deposition of silver from a 1 mM $AgNO_3$ aqueous acidic solution at 20 $\mu A\ cm^{-2}$ was monitored by means of in-situ quartz crystal impedance (QCI) technique, in-situ quartz crystal microbalance (QCM) technique, ex-situ QCI technique and atomic absorption spectroscopy. However, the mass evaluated from the data obtained in the in-situ QCI and QCM measurements on the basis of Sauerbrey equation deviated from intrinsic mass of the deposited silver because of a low deposition efficiency, liquid viscously or rigidly coupled with the resonator and/or stress generated in the deposited layer. Thus one must pay attention to these factors when one calibrates a quartz crystal microbalance on the basis of electrochemical deposition of a metal. In-situ QCI method utilizing a network analyzer is shown to be a powerful technique for simultaneous and qualitative monitoring of mass and surface structure changes. For the quantitative mass measurements, the mass sensitivity must be calibrated using another direct method such as atomic absorption spectroscopy.

In the last decade, many researchers have used quartz crystal resonators to examine the electrode reaction dynamics.[1] The analytical techniques using a quartz crystal resonator can be divided into an active method and a passive method. In the active method,[1] which is known as quartz crystal microbalance (QCM) technique, a quartz crystal itself is made to oscillate spontaneously and the oscillation frequency is counted using a frequency counter. On the other hand, in the passive method,[1,2] which we call the quartz crystal impedance (QCI) method herein, ac voltage is applied to a quartz crystal and an impedance-frequency spectrum is obtained.

The QCM technique has been used to analyze deposition and dissolution processes on an electrode[3—5] and redox processes of modified electrodes.[6,7] In most of these studies, the QCM technique has been used to measure mass loading on an electrode, as can be seen from its name. Indeed, the measured frequency, which is the only parameter obtainable in this method, has a linear relation with the mass increase of a layer adhering to the resonator as long as the layer is rigid and thin enough, as shown by the Sauerbrey equation (Eq. 1):[8]

$$\Delta f = -k\Delta m, \tag{1}$$

where Δf and Δm are changes in the oscillation frequency and mass of a resonator, respectively, and k a proportionality constant. However, the frequency of the QCM is sensitive not only to mass of the adhesion layer, but also to the density, viscosity, elasticity, stress, surface roughness and so forth of the layer,[1,2] so that rigorous mass evaluation is difficult in the cases where some of these parameters change.

On the other hand, in the QCI method, one can obtain an impedance-frequency spectrum as described above. A quartz crystal resonator is electrically equivalent to the electric circuit shown in Fig. 1A. The four components in the circuit: L_1, C_1, R_1, and C_0can be uniquely evaluated from the impedance-frequency spectrum and the spectrum can be reproduced from the set of the evaluated components. Since four parameters can thus be evaluated, the QCI method gives more detailed information than the QCM method. Among the parameters, R_1 corresponds to a loss of oscillation energy. Since the loss of the oscillation energy depends on the rigidity of a film adhering to the resonator, the parameter R_1 is considered as an index of the film rigidity. The QCI method is thus used for examining the film rigidity to judge whether the Sauerbrey equation is applicable to a given system.[7,9] Further, swelling behavior[10—14] including phase transition[12—14] of a film is also detected as a change in the parameter R_1. In a liquid phase, the oscillation energy loss and thereby the parameter R_1 depend also on topography and affinity of the electrode surface to the liquid.[15,16] Increases in the roughness and solvophilicity of the resonator surface result in an increase in amount of liquid oscillating with the resonator, which causes an oscillation energy loss. Therefore, R_1 should be measured even for a rigid film for rigorous mass evaluation.

At present, most QCI measurements are performed

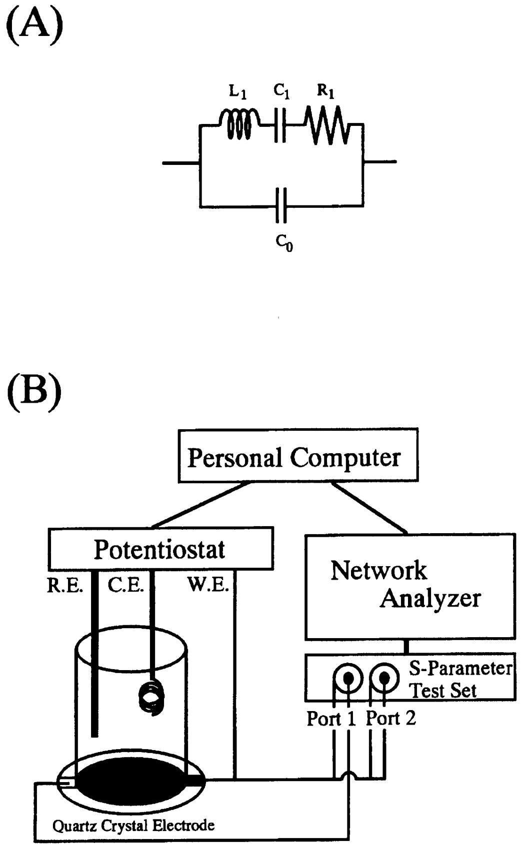

Fig. 1. (A) Electrical equivalent circuit for an AT-cut quartz crystal resonator. (B) Schematic depiction of the experimental apparatus for the in-situ electrochemical quartz crystal impedance measurements.

using an impedance analyzer. However, it takes a few minutes to obtain one impedance-frequency spectrum; hence, the conventional impedance analyzer is not suitable for in-situ monitoring of dynamic electrochemical processes. Recently, a QCI technique employing a network analyzer, which enables one to obtain impedance spectra every second, has been developed,[17] so that a real-time measurement of the dynamic processes is now possible.[18]

For experimental evaluation of the proportionality constant k (Eq. 1), electrochemical deposition of a metal, such as silver, is employed[3] in many cases, because the metal layer is sufficiently rigid. However, roughness of the deposited metal surface often increases with increasing metal thickness. Further, a deposited metal layer can be porous like platinum black under a certain condition. Electrolyte oscillating with the resonator and electrolyte trapped in the pores may lead to overestimation of mass. Stress generated in the deposited film will also lead to overestimation, in the case of AT-cut quartz crystal.[19] Furthermore, deposition efficiency lower than unity will lead to underestimation. In the present work, these factors were examined for silver deposition under conditions where a rough layer is formed, by means of in-situ QCM technique, in-situ QCI technique using a network analyzer, ex-situ QCI technique using an impedance analyzer, atomic absorption spectroscopy (AAS) and scanning electron microscopy (SEM).

Experimental

Materials. Quartz crystal resonators coated with gold electrodes (5 MHz, AT-cut) were prepared as described previously.[20] Electrochemically and piezoelectrically active geometrical areas were 0.503 and 0.283 cm^2. Reagents of analytical grade and double-distilled water was used for all the experiments.

Electrodeposition of Silver. Silver was electrochemically deposited on gold from a 0.2 M $\mathrm{Na_2SO_4}$ aqueous solution (pH 1.0, adjusted using $\mathrm{H_2SO_4}$) (1 M=1 $\mathrm{mol\,dm^{-3}}$) containing 1 mM $\mathrm{AgNO_3}$ using a potentiostat (PS-07, Toho Technical Research, Japan) at a constant current density (20 $\mu\mathrm{A\,cm^{-2}}$). Silver and platinum wires were employed as reference and counter electrodes, respectively.

In-Situ QCI Measurements. Figure 1B shows a block diagram of the in-situ electrochemical QCI measurement system. In the network analysis, voltage transmitted to and reflected from the quartz crystal is measured as reflection and transmission coefficients (scattering parameters). Measurements were carried out employing a network analyzer (HP8753C, Hewlett Packard) and an S-parameter test set (HP85046A, Hewlett Packard) in the course of the electrolytic deposition of silver. An S-parameter test set enables a simultaneous measurement of reflection and transmission coefficients. An electrode potential of the electrochemically active electrode of the quartz crystal was applied through port 1 of the S-parameter test set (Fig. 1B). Admittance Y, which is the reciprocal of impedance, of a quartz crystal was calculated from an output reflection coefficient (S_{22}) for port 2 of the S-parameter test set, using the following equation:

$$Y=(1-S_{22})/(1+S_{22}). \tag{2}$$

Impedance spectra were obtained every 5 s. Each spectrum, which can be obtained in ca. 1 s, consists of impedance data of 401 data points (i.e., impedance data were obtained at 401 different frequencies), and the interval of the data points was 50 Hz. All the impedance data and an electrode potential were transferred to a personal computer (PC-9801DS, NEC, Japan) after each measurement (i.e., every 5 s). A resonant frequency ($=1/2\pi(L_1C_1)^{1/2}$) and an R_1 value were evaluated from each spectrum. The separation of L_1 and C_1 from the resonant frequency is somewhat difficult for our present equipment, so that we evaluated mass from the resonant frequency.

In-Situ QCM Measurements. A quartz crystal resonator was oscillated using a TTL oscillator (built-in-house) in the course of the silver deposition and the frequency was measured using a frequency counter (HP5334B, Hewlett Packard) every 0.5 s. The measured electrode potential and the frequency were transferred to a personal computer.

Ex-Situ QCI Measurements. Ex-situ QCI measurements of a silver-deposited quartz crystal resonator were performed in air by the use of an impedance analyzer (HP 4192A, Hewlett Packard). Prior to a measurement, the electrode surface was thoroughly rinsed with water and dried up in an oven at ca. 50 °C for 15 min.

AAS Measurements. Gold electrodes coated on glass plates were used for AAS measurements. Prior to a measurement, the electrode surface was thoroughly rinsed with water and dried in an oven at ca. 50 °C for 15 min. Then, silver deposited on the electrode was completely dissolved in aqueous nitric acid and diluted with water. Each solution thus obtained was measured with an atomic absorption spectrometer (170-30, Hitachi, Japan), and the amount of silver was determined from a calibration curve.

SEM Analysis of the Electrode Surface. Each electrode surface, which had been rinsed and dried as mentioned above, was observed using a scanning electron microscope (H-700H, Hitachi, Japan).

Results and Discussion

Mass of the Deposited Silver. Silver was electrochemically deposited on a gold electrode of a quartz crystal resonator at 20 µA cm^{-2}. In the course of the deposition, in-situ QCI or in-situ QCM measurements were performed. Figure 2 shows conductance-frequency spectra of the resonator obtained using a network analyzer at 0 s (when the deposition was started), 1000 s and 2000 s. The resonant frequency, which gives the maximum conductance, decreased with time passage; the electrode mass increased as silver was deposited. The R_1 value also changed (discussed below), but the C_0 value showed no significant change. The mass changes were then calculated from the frequency changes observed in the in-situ QCI and QCM measurements on the basis of Eq. 1 (Fig. 3). The proportionality constant k used here was theoretically evaluated from the shear modulus and density of quartz as 17.7 ng cm^{-2} Hz. The mass changes obtained by means of in-situ QCM (M_{isQCM}) were in agreement with those obtained by means of in-situ QCI (M_{isQCI}), within the experimental error. The evaluated mass was larger than the theoretical mass expected from the charge passed assuming 100% deposition efficiency (M_{theo}, dashed line in Fig. 3). As described above, the liquid oscillating with the resonator, liquid or salts trapped in the deposited silver, and/or stress generated in the silver are responsible for the mass appearing to be larger than the theoretical value. This will be further discussed below.

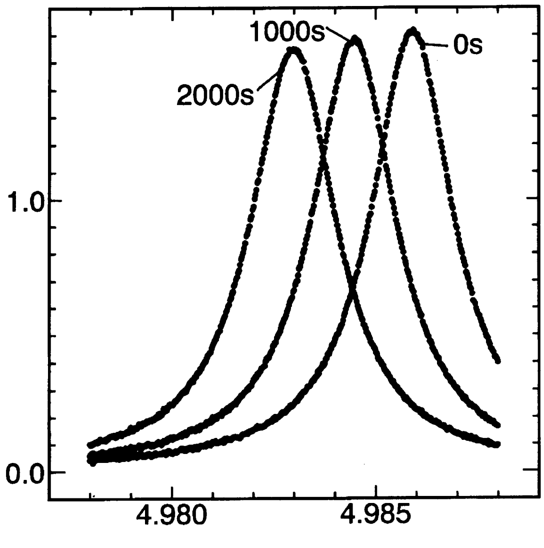

Fig. 2. Typical conductance spectra obtained by means of in-situ QCI for silver deposition at 0, 1000, and 2000 s after the deposition was started.

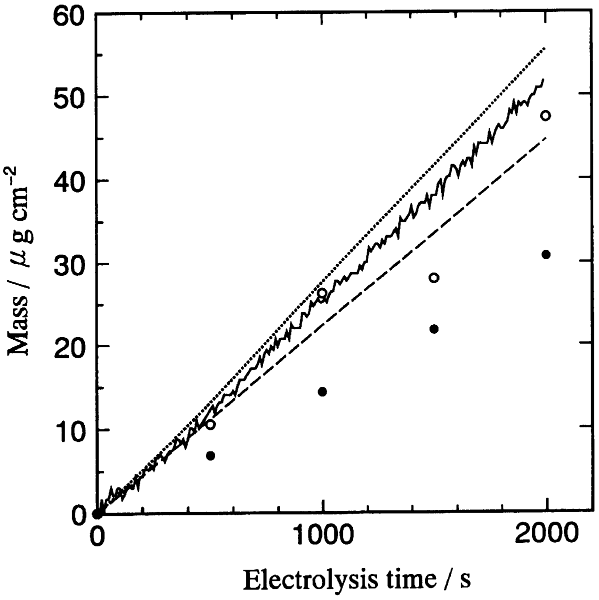

Fig. 3. Plots of the electrode mass change evaluated by means of in-situ QCI (M_{isQCI}; —), in-situ QCM (M_{isQCM}; ····), ex-situ QCI (M_{esQCI}; ○) and AAS (M_{AAS}; ●) against the electrolysis time. Theoretically expected mass is also plotted (M_{theo}; ---).

Ex-situ QCI and AAS measurements were also conducted in air every 500 s; evaluated mass changes are also plotted in Fig. 3. The mass of the deposited silver evaluated by means of ex-situ QCI (M_{esQCI}) has relatively large errors, because four independent resonators were used for the measurements at 500, 1000, 1500, and 2000 s. The M_{esQCI} values were smaller than those evaluated by the in-situ methods (M_{isQCM} and M_{isQCI}). This must be due to the effects of electrolyte, namely the liquid oscillating with the resonator and/or the liquid trapped in pores of the deposited silver, because these effects cannot be considered in the ex-situ experiments.

The M_{esQCI} values agreed with the theoretical values within the experimental error. However, the values obtained by means of AAS (M_{AAS}) were smaller than the M_{esQCI} and M_{theo} values. That is, intrinsic deposition efficiency of the present system was smaller than unity (ca. 66% from the AAS results); this indicates that not all of the reduced silver was deposited on the electrode surface and/or that a part of the deposited silver was detached from the electrode. That the M_{esQCI} values were larger than M_{AAS} values means that stress was generated in the deposited silver or liquid or salts were trapped in the silver, even after the film was dried. That is, M_{esQCI} values close to M_{theo} values do not mean that M_{esQCI} reflects the net mass of the deposited silver.

Surface Roughness of the Deposited Silver. As mentioned above, the differences between M_{esQCI} values and M_{isQCI} values or M_{isQCM} values must arise from some mass of the liquid oscillating with the resonator and/or mass of the liquid trapped in pores of the deposited silver. Most of the liquid oscillating with the resonator is viscously coupled with the resonator, hence the parameter R_1 in the equivalent circuit, which corresponds to the loss of oscillation energy, increases as the amount of the oscillating liquid increases. On the other hand, most of the liquid trapped in the pores is rigidly coupled with the resonator; hence, it may not affect the parameter R_1.

Figure 4 shows typical changes in the parameter R_1 observed in the in-situ QCI experiments. As can be seen, the R_1 value increased as silver was deposited; the amount of the liquid oscillating with the resonator increased. In general, the oscillating liquid increases with increasing surface roughness and increasing surface solvophilicity. Therefore, surface roughness and/or solvophilicity of the deposited silver layer must have increased with increasing silver thickness. Between the surface roughness and solvophilicity, the latter seems difficult to change in the course of the deposition. On the other hand, roughness of the metal surface sometimes increases during electrolytic deposition, under the diffusion-limited condition, because a protrusion is advantageous for the supply of metal ions while a dent is not. In the present galvanostatic electrolysis, stirring of the solution made the electrode potential more positive; diffusion of silver cation limited the deposition rate. Therefore, the surface roughness is expected to increase. Indeed, an increase in roughness during silver deposition was observed by means of scanning electron microscopy. In many cases, the R_1 increase was small at the initial stage of the deposition (Fig. 4). This may be because a small change in the roughness is not reflected by a detectable change in the R_1 value.

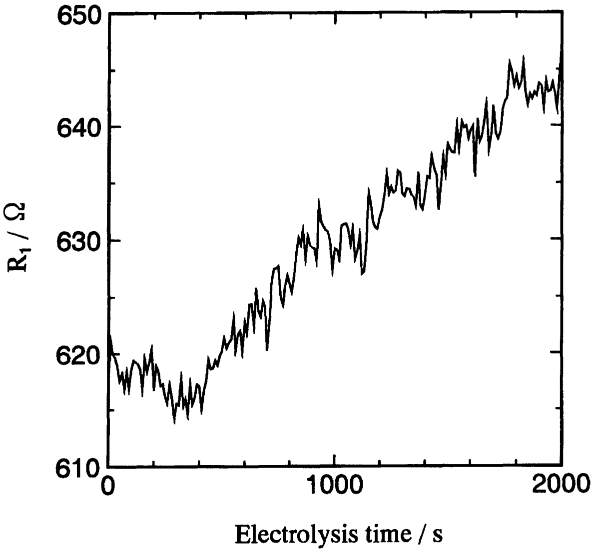

Fig. 4. Typical change in the parameter R_1 for the quartz crystal resonator during the electrochemical deposition of silver.

Thus, now it is clear that the increase in the surface roughness affects the M_{isQCI} and M_{isQCM} values. At present, however, contributions of the roughness changes to those values cannot be determined from changes in the parameter R_1, because the quantitative correlation between a resonant frequency change and an R_1 change arising from a roughness change has not yet been calculated. In contrast, both resonant frequency changes and R_1 changes are known to be proportional to $\Delta(\rho\eta)^{1/2}$ (where ρ and η are density and viscosity, respectively) of liquid in contact with a resonator. We have obtained the correlation between a resonant frequency change and an R_1 change arising from density and viscosity changes using sucrose solutions.[21] On the assumption that such a frequency–R_1 relation is valid for the present case, we estimated the contribution of the roughness increases to the M_{isQCI} and M_{isQCM} values from the changes in the parameter R_1 as about 6%. Though the real contribution of the roughness change is not clear, we should consider that the M_{isQCM} contains at least 6% error coming from the roughness change.

Conclusions

In the present study, we demonstrated that we must pay attention to deposition efficiency, liquid viscously or rigidly coupled with the resonator and stress generated in the deposited layer, when we calibrate a quartz crystal microbalance on the basis of electrochemical deposition of a metal. Even for the ex-situ monitoring, the stress generation and liquid and/or salts trapped in the deposited layer may cause overestimation of mass. As to the in-situ monitoring, increasing surface roughness may also give rise to overestimation. In this case, in-situ QCI method using a network analyzer is useful because both mass and roughness changes can be monitored simultaneously. For the qualitative mass evaluation, however, the mass sensitivity should be calibrated using another direct method such as atomic absorption spectroscopy.

Although apparatus for the QCI method is more expensive than that for the QCM method, one can judge if the quantitative evaluation of mass is possible or not in the QCI measurements. In the QCM monitoring of metal deposition, the Sauerbrey equation has been assumed to hold. As shown here, however, this assumption is not valid in some cases. Therefore, the QCI method is recommended for inorganic systems as well as for organic systems.

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