

## *In-situ* Observation of Solution/electrode Interfaces with Energy Dispersive X-ray Reflectometry Method

Shigeo Sato, Eiichiro Matsubara<sup>1</sup>, Masatoshi Saito<sup>2</sup>  
and Yoshio Waseda<sup>3</sup>

NISSAN ARC, LTD., Yokosuka 237-0061, Japan

Fax: 81-46-867-5814, e-mail: sato\_s@nissan-arc.co.jp

<sup>1</sup> Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Fax: 81-22-215-2076, e-mail: matubara@imr.tohoku.ac.jp

<sup>2</sup> School of Health Sciences, Faculty of Medicine, Niigata University, Niigata 951-8518, Japan

Fax: 81-25-227-0749, e-mail: masaito@clg.niigata-u.ac.jp

<sup>3</sup> Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Fax: 81-22-217-5211, e-mail: waseda@tagen.tohoku.ac.jp

Structural observation of solution/electrode interfaces has been made by the energy dispersive X-ray reflectometry (ED-XR) method. This ED-XR method with high flux white X-rays makes long accumulation time possible, because no monochromator and no angular motion are required. In addition, serious problem due to absorption of X-rays with an upper solution layer on the electrodes can be overcome by the use of high energy X-rays (20-45 keV). These merits enable us to carry out X-ray reflectivity measurement of surfaces in solution.

Surface roughness of mercury in aqueous solution was successfully investigated when changing the potential applied to the mercury in solution with different electrolyte. Direct monitor of density variation in electroplating was also tested.

Key words: roughness, mercury surface, potential, density, electroplating

### 1. INTRODUCTION

Adsorption of ions or deposition of atoms occurs on the electrode surfaces in liquid solution. Understanding these basic processes is of fundamental importance from both the basic science and the applied engineering point of view. However, only a few experimental data on the structure of the electrode surfaces are available because it is very difficult to obtain such information directly. Therefore, most of the structural information of the electrode surfaces are based on thermodynamic consideration[1].

Thickness and density of films, roughness of surface and interface can be evaluated by the X-ray reflectivity method. For example, the density variation across a vapor/liquid interface[2-4] and the surface density, roughness and thickness of solid surface[5, 6] have been recently determined by this method. Although the X-ray reflectivity method is, in principle, applicable to the liquid/electrode interfaces, it is not an easy task. Main reason is serious absorption of X-ray intensity due to the long path length of liquid on the electrode. Therefore, X-ray reflectivity measurements for a system including liquid are still limited for a small number of cases using a synchrotron radiation source[7, 8].

In the general X-ray reflectivity measurements, monochromatic X-ray is used for the incident beam, and the scattering vector is changed by controlling both the incident and exit angles. This method is frequently called the angle dispersive X-ray reflectometry (AD-XR) method. On the other hand, the scattering vector can be changed by energy of X-rays. In this case, white X-rays are applied to a sample at a fixed angle and

the reflected X-rays are measured as a function of energy. Then, this method is referred to the energy dispersive X-ray reflectometry (ED-XR) method. Recently, there are some selected examples with respect to the *in-situ* observation of thin film growth[9, 10] using this method.

The following merits of the ED-XR method are given.

- 1) Since a single crystal monochromator is not required, we are free with severe reduction in intensity of the incident X-rays.
- 2) The use of white X-rays allows us to use X-rays with higher energy of 20-45 keV, so that the X-ray reflectivity measurement for a system including an upper liquid layer can be made without the intense X-ray source.
- 3) Since no angular motion of a goniometer is required during one measurement, this results in free from danger due to fluctuations in the source intensity. Sufficiently enough time for detecting weak intensity can also be allocated because of the parallel counting of photons with different energies.

These characteristic features of the ED-XR method are suitable for *in-situ* observation of solution/electrode interface.

The main purpose of this work is to show the usefulness and validity of the ED-XR method by measuring variation in the solution/mercury interface when changing the applied potential or contacting solutions will be described. *In-situ* observation of electroplating of density variation during deposition of

nickel on iron electrode surface will also be described.

## 2. EXPERIMENTAL

Schematic diagram of the apparatus in the present ED-XR measurements is shown in Fig. 1 (a). White X-ray is generated from a rotating tungsten anode operated with fine focus of 50 kV and 80 mA. The incident angle  $\alpha$  for a horizontal mercury surface is precisely adjusted by changing heights of two slits  $S_1$  (0.04 mm) and  $S_2$  (0.04 mm) placed on a tilting stage supported by two height controllers denoted by  $a$  and  $b$ . Similarly, the take-off angle of reflected beams  $\alpha'$  is defined with a slit  $S_3$  (0.02 mm) mounted on a stage supported by two height controllers  $c$  and  $d$ . The height of the interface is also changed with another height controller  $e$ . The precision of incident angle of the incident beam in this method is  $1.4 \times 10^{-3}$  mrad. Reflected X-ray from a sample surface is collected as a function of X-ray energy with a pure germanium solid state detector placed behind the slit  $S_3$ .

The sample cell used in this work is provided in Fig. 1 (b). In order to obtain a sufficiently flat mercury surface, the size of trough is set in 40 mm square. This length is almost equal to the distance of beam path of both incident and reflected X-rays through the solution above the electrode surface. The kapton film is used for the windows of both sides of the X-ray pass. The potential on the mercury or the iron electrode was controlled by the potentiogalvanostat through the Ag/AgCl standard electrode.

For measuring one X-ray reflectivity profile, three spectra were collected. At first, the spectrum of the incident beam passing through solution was measured. Secondly, the spectrum of reflected X-ray was obtained with respect to the surface or interface of interest. Thirdly, scattering intensity from solution alone was collected without mercury or iron electrode. The escape correction was carried out to all these spectra. The third spectrum is subtracted from the reflected X-ray spectrum so as to extract scattering from the surface or interface itself. The reflectivity profile as a function of energy can be estimated by dividing the corrected reflected intensity profile with that of the incident X-rays.

## 3. RESULTS AND DISCUSSION

### 3.1 Mercury surface in water

The reflectivity profile of mercury surface in water is shown in Fig. 2. The angles  $\alpha$  and  $\alpha'$  were set at 2.09 mrad for the present ED-XR measurements. The surface density of mercury in water may be calculated from the following equations:

$$\alpha = \sqrt{2\delta(E_c)}, \quad (1)$$

$$\begin{aligned} \delta(E_c) &= \delta_{\text{mercury}} - \delta_{\text{solution}} \\ &= \frac{(hc)^2 r_e N_A}{2\pi E_c^2} \left( \frac{Z_{\text{mercury}} + f'_{\text{mercury}}}{A_{\text{mercury}}} \rho_{\text{mercury}} \right. \\ &\quad \left. - \frac{\sum_j x_j (Z_{\text{solution},j} + f'_{\text{solution},j})}{\sum_j x_j A_{\text{solution},j}} \rho_{\text{sol}} \right), \quad (2) \end{aligned}$$

where  $E_c$  is the critical energy for total reflection,  $r_e$  is the classical electron radius,  $N_A$  is the Avogadro's number,  $\rho$  is the density,  $Z$  is the Thomson scattering factor,  $A$  is the atomic weight,  $x$  is the atomic concentration,  $f'$  is the real part of the anomalous dispersion factor. From eqs. (1) and (2) with the value (30.01 keV) of the critical energy of total reflection for water/mercury interface, the density of mercury surface in contact with water is estimated to be  $13.54 \text{ Mg/m}^3$ , which is identical to the bulk density of mercury at room temperature.

The density variation of water/mercury interface is attributed to the roughness of its interface. The experimental profile of the X-ray reflectivity from the interface may be fitted with root mean square roughness,  $\sigma$ , which is related to the Fresnel reflectivity [2-4, 7] in the following form:

$$R(Q) = \exp(-Q^2 \sigma^2) R_F(Q). \quad (3)$$

where  $Q$  is the scattering vector. By fitting calculation to the experimental curve in Fig. 2, the root mean square roughness of mercury surface in water is estimated to be  $0.4 \pm 0.1 \text{ nm}$ . It is worth mentioning that this value appears to be close to those of water ( $\text{H}_2\text{O}$ ) surface ( $0.32 \text{ nm}$ )[2] or free mercury surface ( $0.5 \text{ nm}$ )[11] previously reported from the X-ray reflectivity measurement.

### 3.2 Solution/mercury interface applied potentials

Surface tension of a mercury electrode is known to change depending on its potential, and it is characterized by showing a maximum value at the electrocapillary maximum,  $E_{\text{ecm}}$ , where the mercury electrode is

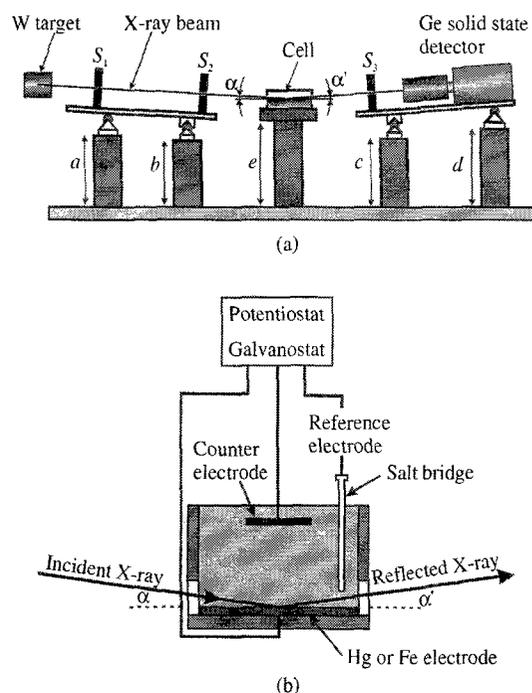


Fig. 1. (a) Schematic diagrams of the ED-XR apparatus. (b) The sample cell to apply the potential to the electrode sample.

electrically neutral. This phenomenon is interpreted by taking into account of ionic adsorption in aqueous solution. Namely, the anions or cations adsorb on the electrode above or below  $E_{ecm}$ , respectively. In order to examine the effect of potential on the mercury surface roughness, X-ray reflectivity measurements were carried out.

The  $E_{ecm}$  for the mercury electrode in KCl (0.1 mol/l) aqueous solution is -0.704 V versus Ag/AgCl[12]. Figure 3 shows the reflectivity profiles obtained under the different potential of 0.0, -0.7 and -1.5 V. The values of  $\sigma$  is estimated to be  $0.4 \pm 0.1$  nm for the case with potential of -1.5 V and  $0.6 \pm 0.1$  nm for the case with potential of 0.0 and -0.7 V. In case of the potential of -1.5 V, the value of  $\sigma$  is identical to that ( $0.4 \pm 0.1$  nm) of the free mercury surface in water.

To investigate the effect of electrolytes on the surface roughness of mercury, X-ray reflectivity measurements of mercury surfaces were made in KBr,  $K_2SO_4$  and  $K_2CO_3$  (0.1 mol/l) aqueous solution. Figure 4 shows the results obtained for cases where the applied potential to the mercury electrode is set at 0.0 V. This condition is quite likely to stick different anions on mercury surface[12]. It has been confirmed from these results that the value of  $\sigma$  is described in the range between 0.5 and 0.6 nm when changing anions. Then, the present authors rather maintain the view that the applied potential or the kind of adsorbed ions to the mercury surface does not significantly affect on the surface roughness of mercury.

### 3.3 In-situ observation of surface density variation during electroplating

Iron polycrystalline electrode was prepared by mechanical polishing to optical flat.  $NiSO_4$  aqueous solution of 0.1 mol/l was chosen to electroplate nickel on the electrode. Electroplating was made under galvanostatic electrolysis of -8.9 mA[11]. The incident and reflection angles were fixed at 1.57 mrad for the present measurements.

Figure 5 shows the reflectivity profiles of the  $NiSO_4$

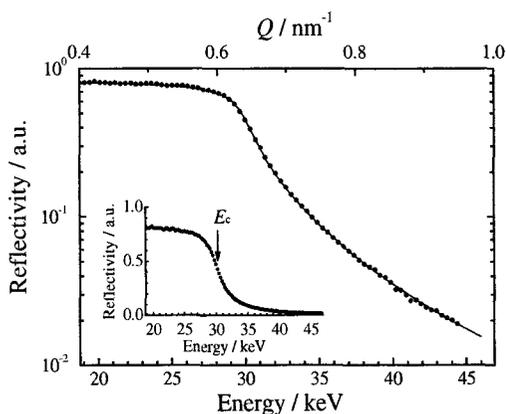


Fig. 2. X-ray reflectivity profile from water/mercury interface (solid dot). The theoretical curve is shown with solid line. The inset represents the X-ray reflectivity altered in the linear scale.

(0.1 mol/l)/Fe electrode interface observed after electroplating for zero, 300, 600 s. The shape of the reflection curve in the close vicinity of the critical energy is broad due to the poor flatness of the Fe electrode surface. However, the critical energy for total reflection can be qualitatively defined from the minimum point of the differentiation curve of the reflection curve. The critical energies for total reflection,  $E_c$ , after electroplating for zero, 300, 600 s are 32.0, 32.7 and 35.2 keV, respectively. The resultant surface density values for the cases with electroplating time of zero, 300 and 600 s are 7.7, 8.0 and 8.8  $Mg/m^3$ , respectively. In calculating these densities, the composition of electrode surface was assumed to be iron for zero second and nickel for 300 and 600 s. It may safely be said that the value for the first case (zero s) corresponds to the bulk density of iron ( $7.86 Mg/m^3$ ). On the other hand, the value for the 600 s case is close to the bulk density ( $8.85 Mg/m^3$ ) of nickel.

The penetration depth around the critical energy is several tens nm, and then the thickness of the 600 s case is estimated to be more than several tens nms. On the other hand, the surface density of the case with electroplating time of 300 s is smaller than the bulk density of nickel. This clearly indicates that the estimated density value corresponds to the mixed state of the upper nickel layer and the iron substrate. Finally, it should be mentioned that no oscillations appear in the reflectivity profiles of Fig. 5 in spite of the existence of the nickel layer on the iron substrate. This is attributed to the poor flatness of the surface.

### 4. CONCLUDING REMARKS

The characterization of electrode surfaces in solution was successfully carried out by the ED-XR method. The results are summarized as follows.

- (1) The surface roughness of mercury in water is 0.4 nm, which is almost identical to that of the free mercury case.
- (2) The applied potential or the kind of adsorbed ions to the mercury surface does not significantly affect on the

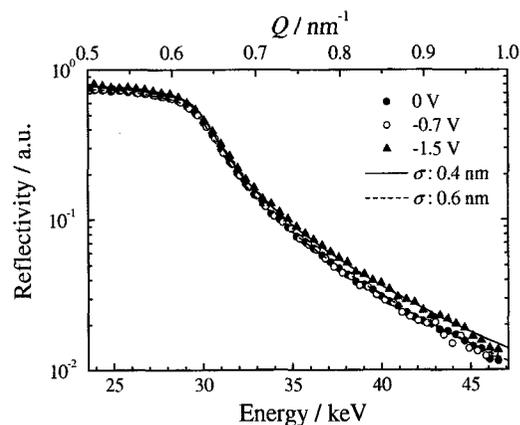


Fig. 3. X-ray reflectivity profiles of KCl (0.1 mol/l)/mercury interface. The X-ray reflectivity profiles given by solid dot, open circle and triangle denote the results measured by applying potential of 0.0, -0.7 and -1.5 V vs. Ag/AgCl on mercury, respectively.

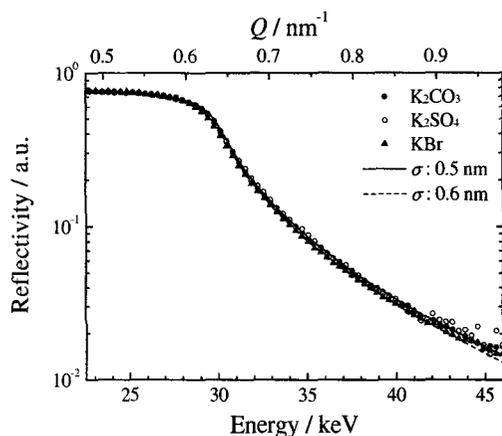


Fig. 4. X-ray reflectivity profiles of mercury surface in contacting with  $K_2CO_3$ ,  $K_2SO_4$  and  $KBr$  (0.1 mol/l) aqueous solution. The potential was applied to the mercury to make anions absorb on it.

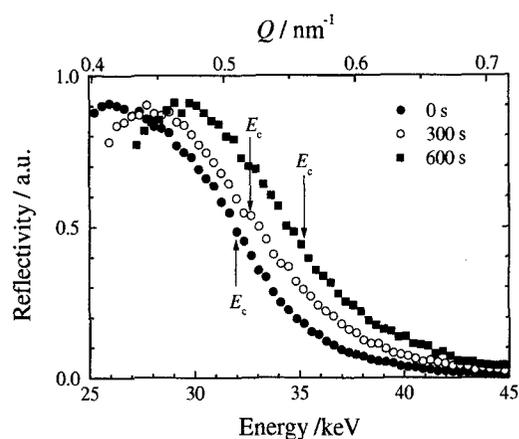


Fig. 5. X-ray reflectivity profiles of  $NiSO_4$  (0.1 mol/l)/Fe electrode interface. The X-ray reflectivity profiles given by solid dot, open circle and square denote the results measured after electroplating for 0, 300 and 600 s, respectively.

surface roughness of mercury.

(3) The ED-XR method appears to be quite useful for the *in-situ* observation of density variation in electroplating.

The accuracy of roughness obtained from the ED-XR method is considered to be sufficiently enough for the present purpose, because the dynamic range of reflectance was as small as a factor of two in comparison to the AD-XR case. Nevertheless, the ED-XR measurements at several fixed angles enable us to extend the range of scattering vector.

Taken from all results in this work, it would be very interesting to extend the ED-XR to other systems of liquid/solid or liquid/liquid interfaces.

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