Development of New In-House Grazing X-ray Reflection System for Analyzing Liquid Surface and Interface

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An in-house grazing X-ray reflection (GXR) apparatus has been newly built for studying the liquid surface, and the liquid-solid and liquid-liquid interfaces. This apparatus consists of a high flux rotating anode X-ray generator, pairs of slits for incident and diffracted beams, a channel-cut Ge 440 crystal monochromator and a double-axis diffractometer. This system was tested by measuring X-ray reflectivity profiles from free surface of water or mercury, and the water-mercury interface.

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I. Introduction

The grazing incidence X-ray scattering (hereafter, referred to as GIXS) method has been applied for studying surface structures of various substances. Density profiles and some interesting features of the surface were obtained in solid films⁽¹⁾⁻⁽³⁾, liquid crystals⁽⁴⁾⁻⁽⁶⁾ and water⁽⁷⁾ by analyzing an experimental reflectivity curve. An in-plane atomic structure of a solid or liquid surface was also determined by measuring the out-of-reflection-plane diffraction under the total external reflection condition⁽⁸⁾. Similarly, an interface structure with different refractive indices was obtained by totally refracting X-ray beams at the interface⁽⁹⁾.

The structure of the electrode-solution interface has long been studied and some models for the interface were proposed⁽¹⁰⁾. Recently, observation of the electrode-solution interface by the atomic force microscopy (AFM) has also been carried out⁽¹¹⁾. However, our understanding of their surface and interface is still far from complete.

With these facts in mind, an in-house grazing X-ray reflection (hereafter, referred to as GXR) apparatus has been newly built for structural studies of the surface of solution and the electrode-solution interface by coupling the conventional rotating-anode X-ray generator. In this paper, we will describe this new GXR apparatus and show its usefulness by measuring the reflectivity profiles of free surfaces of water and mercury and the water-mercury interface.

II. Experimental

A particular feature and the difficulty for designing the

present GXR apparatus is that a whole diffraction geometry should be arranged in the horizontal plane since the liquid surface or liquid-liquid interface is strictly horizontal. The newly developed system is shown in Fig. 1(a). Each part of this system is explained in the schematic drawing of Fig. 1(b). Divergence from a point focus on the target in the high-flux rotating anode generator is much larger than the maximum glancing angle of about 0.4° ($\cong 7$ mrad) for the present GXR measurement. Heights of the three slits S_1 , S_2 and S_3 located on the tilting stage are adjusted by the two lifts e and f in Fig. 1, so that a part of a relatively large divergent beam from the target is incident at a precise glancing angle α on a horizontal liquid surface or interface. Similarly, the take-off angle of the reflected beam or the surface diffraction α' is defined by two slits S_4 and S_5 whose heights are adjusted by the two lifts h and i in Fig. 1. The sample cell b is mounted on a double crossed swivel stage which is attached on the lift g in Fig. 1. By changing the sample height with the lift g , the incident beam is irradiated the center of the sample with the glancing angles of α and α' for the incident and reflected beams. Since these lifts are moved by stepping motors whose finest step is $0.25 \mu\text{m}$, the values of α and α' are controlled to be within 1.4×10^{-3} and 0.63×10^{-3} mrad, respectively. The counter arm holding two lifts h and i , and slits S_4 and S_5 rotates around the center of the sample stage. This enables us to observe the out-of-reflection-plane diffraction from the liquid surface or interface. The rotating anode X-ray generator (Rigaku RU-300) with a molybdenum target and a high brilliant filament is operated at 4 kW. Monochromatic Mo $K\alpha$ radiation is obtained with a channel-cut Ge 440 crystal so that the monochromatic beams are parallel to the incident one. Intensity of this monochromatic Mo $K\alpha$ radiation measured at various incident angles from 0 to 12.2 mrad is shown in Fig. 2. It is

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(a)

(b)

Fig. 1 The in-house grazing X-ray reflection (GXR) apparatus for studying a liquid surface or liquid-liquid interface. (a) overview and (b) schematic diagram. S_1 through S_3 are the slits for incident beams and S_4 and S_5 the slits for reflected beams. a is the channel cut Ge 440 crystal, b the sample cell, c the scintillation counter, d the swivel stage for the sample cell and j the double axis diffractometer. e through i are the lifts for adjusting the heights of slits and sample cell.

Fig. 2 Intensity distribution of incident X-ray beams from 0 to 12.2 mrad.

easily seen that the intensity distribution of the divergent beam is quite homogeneous in the range of the present measurement. It is worth mentioning that the vibrations of liquid surface in the present system is extremely reduced by using a box of sand and several pairs of rubber sheets and steel plates as absorbers.

III. Results and Discussion

An X-ray reflectivity of a Fe_2O_3 film (thickness: 95 nm) grown on a Si wafer observed by the present GXR system is shown in Fig. 3 together with that obtained by the in-house GIXS⁽¹²⁾ system (hereafter referred to as a conventional GIXS system), where the glancing angle α is adjusted by simply rotating the sample around the axis vertical to the direction of incident beams including the sample surface. Although these two systems are based on the completely different methods for setting the glancing angles, the reflectivity obtained in both systems gives the same critical angle for the Fe_2O_3 film. Incidentally, the critical angle was evaluated from the inflection point in the reflectivity curve. It may also be mentioned that the oscillations due to interference of reflected X-ray beams by coupling the Fe_2O_3 surface with the interface between the Fe_2O_3 film and Si wafer are clearly observed in both reflectivity curves of Fig. 3. Such behavior is rather clearly detected in the data observed by the conventional GIXS system.

The monochromatic Mo $K\alpha$ radiation is obtained by 440 reflection of the channel-cut Ge single crystal in the present GXR system while a Ge 111 single crystal plate is used in the conventional one. Therefore, the better energy resolution is achieved in the present system, although the intensity of the monochromatic beam is extremely reduced. In the actual measurement, the total accumulated counts were much less in comparison with the conventional case. This leads to increase in the experimen-

Fig. 3 Reflectivity profiles for Fe_2O_3 film grown on a Si wafer measured (a) by the present apparatus (circles) and (b) by the conventional GIXS system (crosses).

tal uncertainty due to counting statistics and the somewhat insufficient signal to noise ratio in the present system. This may be a reason why the oscillations cannot be clearly observed in spite of the better energy resolution. Nevertheless, the present authors maintain the view that the capability of the present new GXR system is well-recognized by measuring the reflectivity profile of the Fe_2O_3 film and by finding an good agreement with the data using the conventional GIXS system which uses the completely different method for setting the glancing angles.

The reflectivity for a free surface of water was also measured and the results are given in Fig. 4 together with that by Braslaw *et al.*⁽⁷⁾ Since the reflectivity of Braslaw *et al.* measured with the wavelength of 0.1529 nm, their result is normalized with the wavelength of Mo $K\alpha$ (0.071 nm). The critical angle of total reflection of both profiles exists at 1.26 mrad. In point of this result, close agreement between these two curves is obtained. This clearly indicates that the reflectivity from the liquid surface is also quite accurately determined in the present GXR system. However, the reflectivity curve of the present work appears to be slightly less sharp as that reported by Braslaw *et al.*⁽⁷⁾ This is caused by a small curvature of the water surface mainly arising from a small size of the sample cell used in this measurement. Thus, a sample cell of a larger size was used in the following reflectivity measurement for the mercury surface and the mercury-water interface.

It has been emphasized that the mercury-water interface possesses many unique advantages in the matter of understanding the electrified interface. Interface tension of the mercury electrode was often measured as a function of the potential difference across the interface by many workers⁽¹⁰⁾. Thus, our primary motivation of this work is how the atomic structure of mercury-water interface changes under an applied voltage. We believe that this kind of information can provide us an approach to understand the solution-electrode interface. First, the

Fig. 4 Reflectivity profiles for a free water surface observed (a) by the present system (solid dots) and (b) by Braslaw *et al.*⁽⁷⁾ (circles).

reflectivity of mercury itself was measured. The reflectivity of a free mercury surface is shown in Fig. 5. For two cases; one is Mo $K\alpha$ (0.071 nm) diffracted by Ge (440) plane and the other is the two times larger wavelength of 0.142 nm diffracted by Ge (220). The critical angle is 3.7 mrad for Mo $K\alpha$, from which the surface density of mercury is calculated to be 13.4 Mg/m^3 . This value is very close to that of pure mercury, 13.5 Mg/m^3 . Furthermore, the observed critical angle of mercury for the wavelength of 0.142 nm is twice as large as that for Mo $K\alpha$, which satisfies the proportional relationship between the critical angle and wavelength. The experimental reflectivity profiles quite well coincide with those theoretically evaluated by the method proposed by Parratt⁽¹³⁾. These observations also prove the accuracy of the angular setting for glancing angles in the present system.

Since the incident and reflected X-ray beams with a small glancing angle are heavily absorbed by water, the reflectivity for the mercury-water interface is extremely reduced. Consequently, the thickness of water on mercury must be kept less than 0.5 nm. Because it is difficult to cover mercury surface with a thin water layer, mercury surface is covered by a Kapton film so that a small gap is left between them. Therewith, a thin water layer lies in this gap. In this work, the profiles for two wavelengths of 0.071 nm (Mo $K\alpha$) and 0.142 nm were measured. The resultant reflectivity curves of the mercury-water interface are shown in Fig. 6. The reflectivity for Mo $K\alpha$ (0.071 nm) decreases rapidly at about 1.3 mrad and gradually decays up to 2 mrad. As it has been expected, a similar reflectivity profile is obtained for 0.142 nm at just two times larger scattering angles than those of the Mo $K\alpha$ case. It is worth mentioning that the reflectivity profile for a free water surface in Fig. 4 is sharper than that for water covered by a Kapton film in Fig. 6. This could be qualitatively explained by the fact that the surface of water layer covered by the Kapton film is not as flat as the free water surface. As it is clearly seen in the inserted

Fig. 5 Reflectivity profiles for a free mercury surface with wavelengths of (a) Mo $K\alpha$ (0.071 nm) (squares) and (b) 0.142 nm (circles). The solid curves are the reflectivity profiles calculated by the method proposed by Parratt⁽¹³⁾.

Fig. 6 Reflectivity profiles for a mercury-water interface with wavelengths of (a) Mo K α (0.071 nm) (solid dots) and (b) 0.142 nm (circles). The inserted figure corresponds to a part of the enlarged reflectivity profile with Mo K α .

profile of Fig. 6 where a part of the reflectivity profile for Mo K α at about 4 mrad is enlarged, the reflectivity decreases again at about 3.7 mrad. This is attributed to the reflection at the water-mercury interface. The results of Figs. 5 and 6 again clearly suggest that the new GXR apparatus works well and enable us to provide valuable information for water-mercury interface through their reflectivity measurements.

There are few applications of the GXR method to structural studies of a liquid-liquid interface within the best knowledge of the present authors. For this reason, we have developed a new in-house GXR system for studying a liquid surface and a liquid-liquid interface and its usefulness and validity were well demonstrated as exemplified by some selected measurements from the free surfaces of water and mercury and the water-mercury interface. It is also found in this work that the intensity of incident X-rays should be improved, for example, by replacing air by He gas in a beam path. However, the

potential capability of this new GXR system may not be overemphasized. It is rather surprisingly effective for studying the atomic scale structures of a liquids surface and a liquid-liquid interface. Thus, we are now carrying out some further measurements of reflectivity and out-of-reflection-plane diffraction from a mercury-water interface under various applied voltages in order to obtain new knowledge of the surface structure of the mercury electrode.

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