

## Development of an *in-situ* X-ray diffraction system for observation of electrodeposition of metallic layers

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In order to study the dynamic phenomena of electrodeposition of metallic layers, an *in situ* X-ray diffraction system has been newly developed using an electrochemical cell and an image-plate detector. Electrodeposition of Zn on an Fe(100) single-crystal surface with a current density at  $0.5 \text{ A cm}^{-2}$  was demonstrated in this study. Time-resolved diffraction patterns were obtained by scanning the image plate. It was found that Zn(101) layers were mainly formed from the initial stage of deposition and grew continuously on this substrate. Growth of other layers, such as Zn(103), Zn(110) and Zn(102), were also detected. On the other hand, Zn(100) and Zn(002) were not observed under this condition.

**Keywords:** *in-situ* observations; electrodeposition; X-ray diffraction.

### 1. Introduction

The electrodeposition method has been widely applied for surface coating of materials. It is well known that the morphology and preferred orientation of deposited metals affect their mechanical and anticorrosive properties and that they are influenced by various process variables, *e.g.* substrate materials, current density and inhibitors *etc.* (Masuko & Tsuda, 1993). Although the electrochemical kinetics and transport properties have been studied intensively, both theoretically and experimentally, direct observation of electrochemical texture growth under the existence of an electrolyte has been elusive up to now.

Some investigators have tried to determine the structures of very thin electrodeposited metals after deposition. For example, the structures of electrochemically deposited monolayers of Pb on Ag(111) and Au(111) were investigated by Samant *et al.* (1988) using grazing-incidence X-ray diffraction. They removed the solution for the measurement and therefore they have not studied dynamic layer growth.

In order to study the dynamic phenomena of electrodeposition, we have newly developed an *in situ* X-ray diffraction system using an electrochemical cell and an image-plate detector. High-brilliance synchrotron radiation was used as the X-ray source to detect such a fast layer growth.

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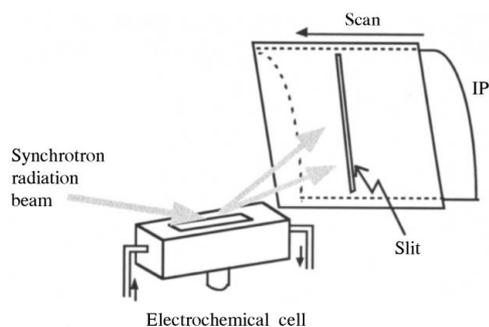
### 2. Experimental

The *in situ* X-ray diffraction system with an electrochemical cell was installed on beamline BL-3A at the Photon Factory, High Energy Accelerator Research Organization (Fig. 1). A monochromated synchrotron radiation X-ray beam of wavelength  $0.06 \text{ nm}$  and size  $3.0 \times 0.7 \text{ mm}$  irradiated the surface of the deposited layers. The image plate was set on the curve-shaped scanning holder. The radius of this holder was fixed to be equal to the distance from the sample to the image plate, which was  $310 \text{ mm}$ . By adopting this geometry, it is easy to calculate the diffraction angle,  $2\theta$ , from the distance in the vertical direction on the recorded image. The X-ray diffraction pattern was recorded continuously on the image plate displaced at a constant speed of  $3.5 \text{ mm s}^{-1}$  behind a slit during deposition. A similar image-plate displacing system has already been reported by Rizzo *et al.* (1995) to study the phase transformation of Fe–Zn.

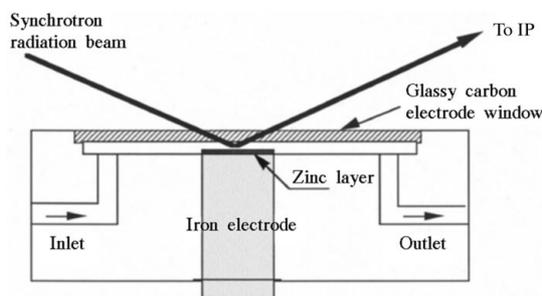
Fig. 2 shows a schematic diagram of the electrochemical cell. This cell was fabricated from a polyvinyl chloride box with a substrate metal electrode and a glassy carbon sheet window. The electrolytic solution used in this study was  $0.5 \text{ M ZnSO}_4$ ,  $0.1 \text{ M Na}_2\text{SO}_4$  and  $0.1 \text{ M H}_2\text{SO}_4$ . An electric current was applied between them. Therefore, the glassy carbon sheet, of thickness  $0.25 \text{ mm}$ , played the roles of both counter electrode and X-ray transparent window at the same time during deposition. The changes in the diffraction pattern with a current density of  $0.5 \text{ A cm}^{-2}$  in  $\sim 30 \text{ s}$  deposition were clearly observed through the window and flowing electrolyte.

### 3. Results and discussion

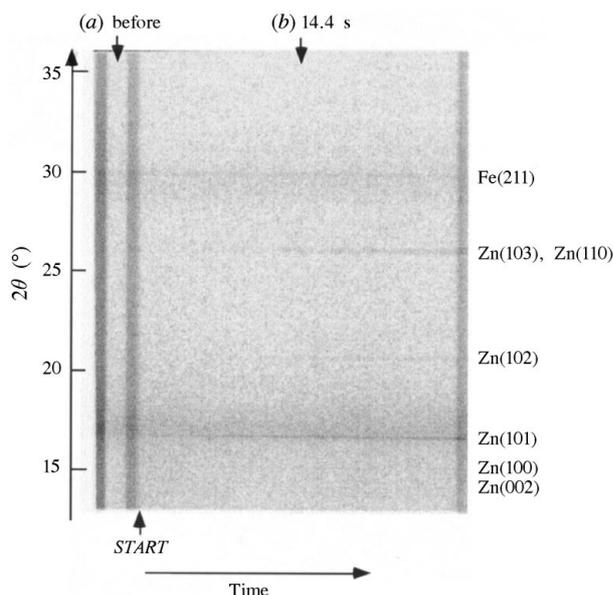
A dynamic study of the electrodeposition of Zn on an Fe(100) single-crystal surface was demonstrated by using this system. An X-ray diffraction pattern recorded on the image plate is shown in Fig. 3. The vertical direction corresponds to the diffraction angle,



**Figure 1**  
Schematic diagram of the *in situ* X-ray diffraction system.

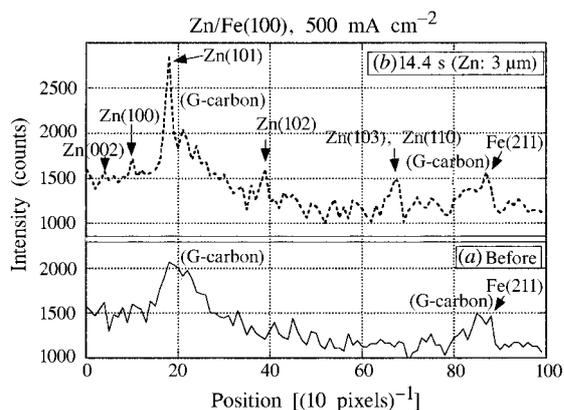


**Figure 2**  
Schematic diagram of the electrochemical cell.



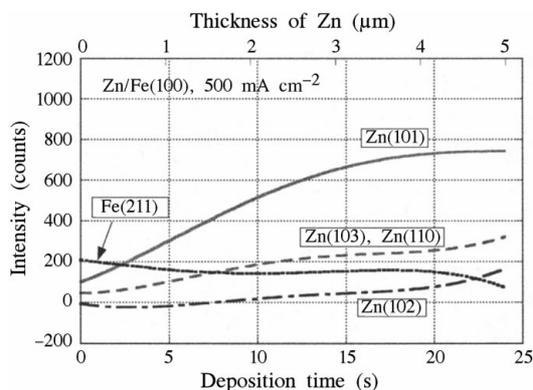
**Figure 3**

Diffraction pattern recorded on the image plate. The vertical direction corresponds to the diffraction angle,  $2\theta$ . Deposition at the 'start' point is marked. The sections (a) and (b) indicate deposition before and after an elapsed time of 14.4 s, respectively.



**Figure 4**

Diffraction patterns at the two sections (a) before deposition and (b) 14.4 s after deposition has commenced, *i.e.* as indicated in Fig. 3. The intensity value is equivalent to the summation of intensities at every  $10 \text{ pixels} \times 10 \text{ pixels}$  area on the image plate.



**Figure 5**

Diffraction intensity changes as a function of time for several planes of Zn and the substrate, which were derived from the pattern shown in Fig. 3.

$2\theta$ . The two-dimensional resolution of the diffracted X-ray intensity was  $100 \mu\text{m} \times 100 \mu\text{m}$  per pixel on the image plate. The 'start' point of the electrodeposition of Zn is indicated in this figure. The increase of the intensities with time for some indexed diffraction lines, which represents the growth of the Zn layer, can be easily seen in this figure. The diffraction peak of Fe(211) was also observed because one equivalent plane of Fe{211} exists near this direction for the Fe(100) surface in this geometry. On the other hand, diffraction lines for typical crystal planes of Zn, *i.e.* Zn(002) and Zn(100), were not clearly observed. This means that high plane-density layers of the *c* and *a* planes could not be grown under this deposition condition. Fig. 4 shows two sections of the image (a) before deposition and (b) after an elapsed time of 14.4 s marked on Fig. 3. Before the deposition, only the diffraction from the Fe substrate and the broad peak from the glassy carbon (G-carbon) window were observed. The thickness of the Zn layer was  $\sim 3 \mu\text{m}$  at the section of (b) *i.e.* after 14.4 s. Several diffraction peaks, especially for Zn(101), were observed besides the diffraction pattern shown in Fig. 4(a). We can analyse the pattern at any section of deposition time by using the intensity data recorded on the image plate.

The changes of the diffraction intensities during the deposition are summarized in Fig. 5. The intensity of Zn(101) increased monotonously in 15 s, which means the thickness of the Zn(101) layers increased almost linearly in this condition. It saturated at the last stage of deposition probably because the X-ray path length becomes comparable with the penetration depth for the Zn layer. Other Zn layers, such as Zn(103), Zn(110) and Zn(102), were also detected during the whole course of deposition. On the other hand, the intensities of Zn(100) or Zn(002) were very weak and hard to analyse (therefore, these are not included in this figure). As for the substrate, the intensity of Fe(211) decreased as the growth of the Zn cover layers took place during deposition.

In conclusion, it was found that the dominant relationship of growth orientation of Zn on the Fe(100) plane is  $\{100\}\text{Fe}/(101)\text{Zn}$  from the first stage to the end of deposition under the deposition current density of  $0.5 \text{ A cm}^{-2}$ .

The preferred orientation of grown layers should depend, however, not only on the orientation of the substrate but also on the current density, *i.e.* the overvoltage, of deposition (Pangarov, 1965). It is easy to change the electrochemical conditions, *e.g.* substrate materials, current density and inhibitors *etc.*, in our electrochemical cell. This system is very useful for the study of dynamic phenomena including the first stage of layer growth of electrodeposition.

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