

In situ Structural Study on Layer-by-layer Deposition of Pt on Au(111) by Resonance Surface X-ray Scattering

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Introduction

Ultra-thin films on foreign metal substrates have been attracting interests because of their unique physical and chemical properties, particularly their electro-catalytic activities. Such high electro-activities are caused by the geometric and electronic structures of the interfacial layers different from those of the bulk [1], and therefore, it is very important to know the interfacial structures with atomic dimensions.

Pt ultra-thin films on foreign metal substrates are expected to be a good electro-catalyst in many reactions. Moreover, Pt is one of the most precious materials so that the loading amount of Pt as an electrocatalyst is expected to reduce. Previously, structural studies of electrochemically deposited Pt ultra-thin layers on a Au(111) single crystal electrode surface have been carried out by several groups [2-4] by scanning tunneling microscopy (STM), but the results were different from each other. While Naohara et al. reported that Pt grows on an atomically flat Au(111) surface in the layer-by-layer mode [2], Waibel et al. [3] and Strbac et al. [4] reported that Pt grows on the Au(111) surface in the islanding mode. We confirmed this difference using surface X-ray scattering (SXS) [5].

The SXS technique is ideal to determine the structure of the metal deposit with atomic precision, but since the atomic number and, therefore, the scattering parameters of Pt are too close to those of Au, the interfacial structure of the Pt layer on the Au substrate cannot be precisely determined from the (00) rod data obtained using the incident energy of 11.271 keV, which is usually used in our SXS studies [6-9]. Thus, we have now demonstrated that the resonance SXS (RSXS) method, in which the incident X-ray energy close to the Pt LIII absorption edge (11.55 keV) is used so that the anomalous scattering parameter effect is utilized [5], is very useful to precisely determine the interfacial structure of the Pt layers prepared on a Au(111) surface. In this report, we monitored the interfacial structure during layer-by-layer deposition of Pt on Au(111) using RSXS *in situ*.

Experimentals

The RSXS measurements during layer-by-layer deposition of Pt on Au(111) were carried out at the BL4C bending magnet beamline at PF. Pt was electrochemically deposited on the Au(111) surface in 0.1 M HClO₄ electrolyte solution containing 0.05 mM PtCl₆²⁻ by negatively scanning the potential from open circuit potential (OCP) to +0.90 V (vs. RHE), by keeping the

potential for several periods and then by disconnecting the electrode from the potentiostat. After that, the spectro-electrochemical cell [8] was set on the diffractometer installed at the BL4C beamline and RSXS measurements were carried out. We selected the incident X-ray energy between 11.4 keV and 11.75 keV in the RSXS measurements. The (00) and (01) rods and incident X-ray energy dependence of the scattering X-ray intensity at various scattering points were measured using these energy [5].

Results and Discussion

Based on the analyses of the (00) and (01) rods (Fig. 1) and incident X-ray energy dependence of the scattering X-ray intensity at various scattering points, the PtCl₆²⁻ ion is adsorbed on the Au(111) surface with a ($\sqrt{7} \times \sqrt{7}$)R19.1° structure at OCP. After keeping the potential at +0.90 V for 2000 s, atomically flat Pt monolayer with a (1×1) structure forms on the Au(111) surface and this monolayer is covered with the adsorbed PtCl₆²⁻ layer with a ($\sqrt{7} \times \sqrt{7}$)R19.1° structure. As proceeding the deposition, Pt grows with a layer-by-layer mode on the Au(111) surface at least until 2 ML.

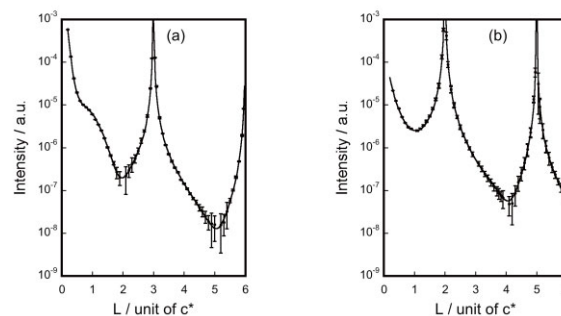


Fig. 1 (a) (00) and (b) (01) rod profiles measured at OCP.

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