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Structures of Pt Ultra-Thin Films on Au(111) Prepared by Self-Terminated Deposition

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1 Introduction

It is very important to construct a pseudomorphic precious metal ultra-thin layers on a foreign metal surface not only for basic science but also for technological application, because they often have high electrocatalytic acitivities [1,2]. Since platinum is one of the most widely used electrocatalysts, it has been expected to prepare the pseudomorphic Pt layers on the foreign metal surface, especially on Au(111) [3-9]. Using underpotential deposition (UPD) and Galvanic replacement techniques, Pt monolayer forms on Au(111) [3,4], but there are no reports, in which preudomorphic Pt monolayer forms, because atomic-atomic distance mismatch between UPD metal and Pt is relatively high. By using resonance surface x-ray scattering (RSXS) technique, we previously succeeded to electrochemically construct the pseudomorphic Pt monolayer on Au(111) by control of electrochemical conditions such as Pt complex concentration, deposition potential, and deposition period [5-7] and its high electrocatalytic activity for oxygen reduction reaction (ORR) was confirmed [10]. Recently, Moffat et al. reported that the atomically controlled Pt monolayer formation on Au(111) by a self-terminating effect of Pt complex ion used as a Pt source [8,9]. However, no one know whether the formed Pt ultra-thin layer is preudomorphic or not, because they used (111) textured Au thin films, not Au(111), as a substrate.

In this report, we investigated the structures of the ultra-thin Pt layers prepared on Au(111) by the self-terminated electrochemical deposition using RSXS.

2 Experiments

Prior to RSXS measurements, Au(111) disk was annealed by a Bunsen gas burner and quenched by dipping it in ultra-pure water [11]. After that, the potential of the Au(111) disk was stepped for 1 or 2 times from open circuit potential (OCP) to ca. -0.5 V (vs. Ag/AgCl), where hydrogen evolution takes place on the Pt surface, in a deaerated buffered electrolyte solution (pH=4.0) containing 3 mM $PtCl_4^{2-}$. After the sample throughly washed with conc. H2SO4 and ultra-pure water and dried with a nitrogen flow, the cyclic voltammetry (CV), angle-resolved x-ray photoelectron spectroscopy (ARXPS), and RSXS measurements were carried out. In the RSXS measurements, incident x-ray energy was employed between 11.35 and 11.8 keV, which include the PtLIII absorption. RSXS measurements were carried out at BL3A/BL4C beamlines in Photon Factory.

3 Results and Discussion

Based on the CV and ARXPS results, it was found Pt coverage, prepared by a single-potential step and double-potential step self-termination, was ca 0.5 ML and 1.0 ML, respectively. From the structure analyses of the RSXS results by fitting the data with the theoretical equation [11,12], while a half Pt monolayer, in which Pt atoms exist at the three-fold hollow cubic close packed (ccp) and hexagonal close packed (hcp) sites with a ratio of 1:1, forms on the Au(111)-(1×1) surface by a single-step self-termination, a pseudomorphic Pt full monolayer, in which all the Pt atoms exist at the three-fold hollow ccp site, forms on Au(111) by a double-step self-termination.

4 Conclusion

Results of the CV, ARXPS, and RSXS measurements showed that a half Pt monolayer and a full pseudomorphic Pt monolayer form on the Au(111)-(1×1) surface by self-terminated electrochemical deposition.

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