

In situ Structural Study of Electrochemically Deposited Pd Layers on Au(111) by Surface X-ray Scattering Measurements

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1. Introduction

Electrochemical metal deposition on metal and semiconductor is important not only for fundamental science but also for various industrial applications. A large number of studies have been carried out to understand the mechanism of electrochemical deposition of metal at an atomic level [1-3].

Recently, we have found that the electrochemical deposition of Pd layers on an Au(111) electrode surface proceeded epitaxially using scanning tunneling microscopy (STM) [4,5]. The spatial resolution of STM, however, is limited while the bond length should be determined within ± 0.01 Å in order to distinguish the atomic distance of Au-Au and Pd-Pd. Surface X-ray scattering (SXS) using synchrotron orbital radiation (SOR) light source which can provide information with higher resolution has recently been applied to electrode/electrolyte interfaces by various groups [6-8]. In this report, we investigated the structure of electrochemically deposited Pd layers on Au(111) by *in situ* SXS measurements.

2. Experiment

Reagent grade H_2SO_4 and H_2PdCl_4 were obtained from Wako Pure Chemicals and used without further purification. A Milli-Q water purification system (Yamato, WQ-500) was used to obtain ultrapure water. An Au(111) single-crystal disk ($\phi = 10$ mm, $d = 5$ mm) was purchased from MaTeck (Germany).

In situ SXS experiments were carried out at the bending magnet beamline BL14B1 at SPring-8. After H_2 flame annealing and cooling under N_2 , the Au(111) disk was set to a specially designed electrochemical X-ray scattering cell, which is made from polychlorotrifluoroethylene (PCTFE). A 6.0 μm thick Mylar film (Chemplex) was used as a window and was set to the cell while keeping the thickness of the solution between the electrode and the window film more than 5 mm. After deaeration by passing N_2 , solution containing 0.1 M H_2SO_4 and 0.01 M K_2PdCl_4 was introduced into the cell while the potential was kept +0.90 V (vs. Ag/AgCl), which is more positive than the UPD potential of Pd at Au(111). Electrochemical deposition of Pd on Au(111) was carried out by scanning a potential for negative direction to +0.50 V and back for positive direction to

+0.55 V, at which neither more cathodic deposition current nor anodic dissolution current was observed. The surface coverage of Pd was calculated by cathodic charge passed during the above treatment. After deposition of Pd, the solution thickness was decreased to less than several tens of μm by deflation and the cell was mounted on a (2+2) type diffractometer (New Port). Incident X-ray energy of 14.952 keV was selected by using Si(311) double crystal monochromator.

3. Results and Discussion

Figure 1 shows crystal truncation rod (CTR) profiles measured along (0,0) and (0,1) rods at 1.0 ML of deposited Pd on Au(111). By fitting the (0,0,L) profile,

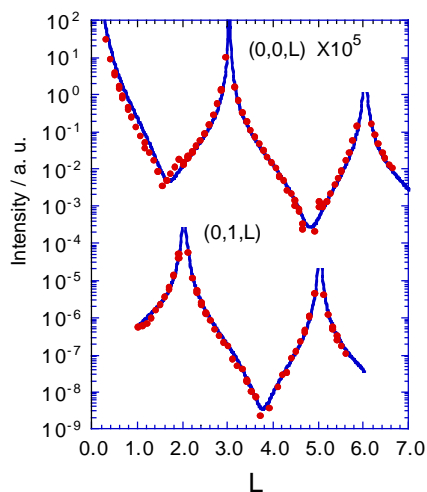


Fig. 1. (0,0,L) and (0,1,L) CTR profiles when 1 ML of Pd was deposited on Au(111). Dots and solid lines are experimental and fitting data, respectively.

the distance between the 1st Pd layer and the top layer of Au(111) was determined to be 2.24 Å, which is less than those of Au-Au bulk (2.36 Å) and Pd-Au bulk (2.27 Å). This result indicates the strong interaction between the 1st Pd and the top Au layer. Fitting of the (0,1,L) profile showed that Pd atoms sit on the fcc sites on Au(111) surface, indicating that the 1st Pd layer is deposited epitaxially. In our previous XRD measurement of more than 70 ML of deposited Pd on Au(111), only the (111) peak of Pd was observed and no other peaks due to Pd such as (200), (220) and (311) were

observed [4,5]. These results indicated that the Pd-Pd distance at more than 70 ML of deposited Pd on Au(111) is the same as that of Pd-Pd bulk (2.75 Å). It was found that the Pd-Pd distance changes from 2.89 Å to 2.75 Å as the deposition proceeds.

Fitting results of (0,0,L) and (0,1,L) CTR profiles at 2 ML of deposited Pd on Au(111) showed that the 2nd Pd layer also deposited epitaxially on the 1st layer of Pd on Au(111), *i.e.*, the in-plane Pd-Pd distance of 2.89 Å.

Figure 2 shows the in-plane diffraction along (H,0) direction at L = 0.6 at 1 and 5 ML of deposited Pd on Au(111). At 1 ML of deposited Pd on Au(111), only one large sharp peak was observed at H = 1.00. This peak position is exactly the same as that of the Au(111) surface, confirming that the lateral atomic distance between Pd atoms in the 1st layer is 2.89 Å. On the other hand, a small peak at K = 1.05 corresponding to the atomic distance of 2.75 Å was observed after 5 ML of Pd was deposited in addition to that at K = 1.00. This result indicates that the lateral atomic distance of Pd atoms at the 5th layer on Au(111) is 2.75 Å, which is the same distance between bulk Pd atoms. The peak at K = 1.05 in the lower K side has a small shoulder, suggesting that the intermediate layers where Pd-Pd distance is between 2.89 Å and 2.75 Å exist at the interface between the 2nd and 5th Pd layers.

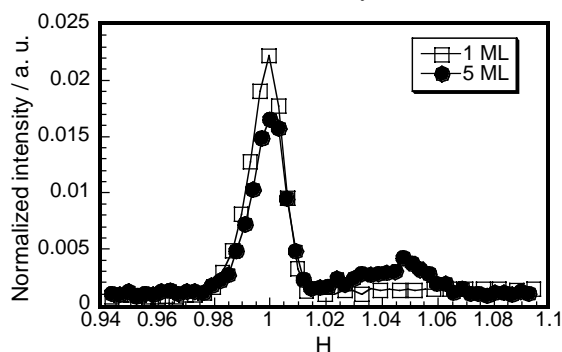


Fig. 2. In-plane diffraction measured along (H,0) direction when 1 (□) and 5 (●) ML of Pd were deposited on Au(111).

4. Conclusion

The structure of electrochemically deposited Pd layers on Au(111) was studied in detail by *in situ* surface X-ray scattering measurements. Deposited 1st and 2nd Pd layers are commensurate with Au(111) surface. In-plane Pd-Pd distance is 2.89 Å at the 1st and 2nd layers of Pd and is 2.75 Å when 5 ML of Pd was deposited on Au(111). In the in-plane diffraction curve, a small shoulder, which suggests that the intermediate layers where Pd-Pd distance is between 2.89 Å and

2.75 Å exist at the interface between the 2nd and 5th Pd layers, was observed.

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