STRUCTURAL DYNAMICS OF SURFACE OXIDATION REACTION AT Au(111) AND Au(100) SINGLE CRYSTAL ELECTRODES USING IN SITU SURFACE X-RAY SCATTERING TECHNIQUE

Toshihiro KONDO, Jun MORITA[†], Kazuya HANAOKA[†], Satoru TAKAKUSAGI[†], Kazuhisa TAMURA[††], Masamitu TAKAHASI[††], Jun-ichiro MIZUKI[††], and Kohei UOSAKI[†]

Department of Chemistry, Faculty of Science, Ochanomizu University, Tokyo 112-8610, JAPAN

[†]Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, JAPAN

[††]Synchrotron Radiation Research Center, Japan Atomic Energy Research Institute, Hyogo 679-5148, JAPAN

We have investigated the interfacial structure of several electrochemical reactions at an atomic level using in situ SXS technique [1-4]. Here we report the structurally dynamic study on the surface oxidation reaction at Au(111) and Au(100) single crystal electrodes/electrolyte solution (50 mM H_2SO_4) interface using in situ SXS technique.

After the H_2 flame annealing, gold single crystal disk was set in the specially designed spectroelectrochemical cell [3]. At 0 V (vs. Ag/AgCl), the electrode surface was touched with deaerated 50 mM H_2SO_4 solution and the potential was scanned to several measuring potentials at a scan rate of 20 mV s^{-1}, then the electrode surface was pushed to the Mylar film (thickness: 6 μm) keeping at those potentials. The thickness of the electrolyte layer between the electrode and the window was estimated to be ca. 30 μm. Potential scan measurement was also carried out in the other configuration, in which the electrolyte layer thickness was several hundreds μm. The cell was mounted on a six-circle diffractometer or κ-type diffractometer, which are installed on a bending-magnet beamline BL4C at the Photon Factory or BL14B1 at the SPring-8, respectively, and in situ SXS measurements were carried out at room temperature. A wavelength 1.100 Å was selected to avoid any fluorescence from the Au substrates.

Figure 1 shows the specular rod profiles measured at 0 V (circle) and +1.40 V (triangle). At 0 V, one dip was observed between the two adjacent bulk Bragg peaks and the data were in good agreement with those calculated with the reconstruction models (solid lines in Fig. 1); ($\sqrt{3} \times 23$) and hexagonal structure at Au(111) and Au(100), respectively. However, at +1.40 V, another deep dip was observed at L = 0.7 and 0.4 at Au(111) and Au(100), respectively. Fitting results (solid lines in Fig. 1) showed that about 1 ML of Au atoms were lifted by ca. 3 Å as a result of the penetrating of the oxygen atoms into the outermost gold layer, i.e., the surface oxide film formation, at the both electrodes.

When the detector position was fixed at L = 0.7 and 0.8 at Au(111) and at L = 0.4 and 0.5 at Au(100), the scattering intensity was measured during the potential scan (Fig. 2). While the intensity at L = 0.7 is larger than that at L = 0.8 at the all potentials we measured at Au(111) (Fig. 2(a)), the intensity at L = 0.4 was less than that at L = 0.5 at the potential range for the gold oxide formation (Fig. 2(b)). These results indicated that the oxide film formation at Au(100) occurs much faster than that at Au(111). This result is consistent with previous SHG result [5].

References

1. M. Takahasi et al., Surf. Sci., 461 (2000) 213.
2. T. Kondo et al., J. Electroanal. Chem., 532 (2002) 201.
3. T. Kondo et al., Electrochim. Acta, 47 (2002) 3075.
4. K. Uosaki et al., “Thin Films; Preparation, Characterization, Applications”, Eds. M. P. Soriaga, J. Stickney, L. A. Bottomley, and Y.-G. Kim, Kluwer Academic/Plenum, New York (2002).
5. T. Awatani, I. Yagi, and K. Uosaki, submitted.

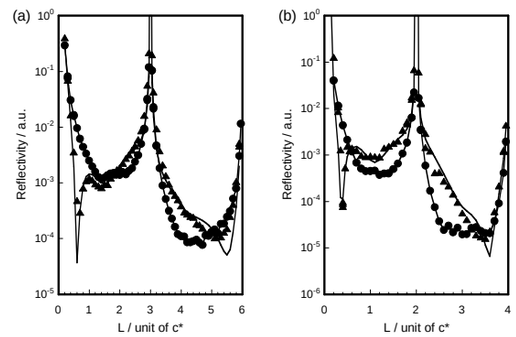

Fig. 1 The specular rod profiles at (a) Au(111) and (b) Au(100). Circles and triangles were measured at 0 V and +1.40 V, respectively. Solid lines are the calculated curves.

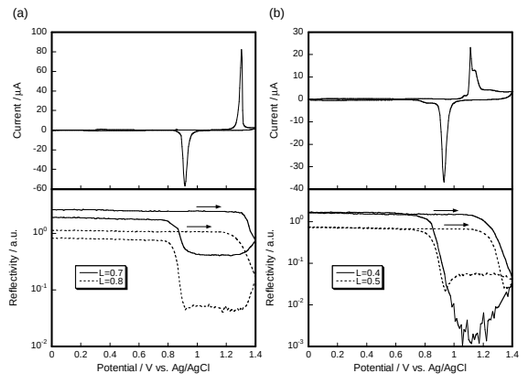

Fig. 2 Cyclic voltammograms and potential dependence of X-ray scattering intensity at (a) Au(111) and (b) Au(100). Solid and dotted lines are L = 0.7 and L = 0.8, respectively, at Au(111) and are L = 0.4 and L = 0.5, respectively, at Au(100).