Reflection Electron Microscopy of Copper Electrocrystallization on Platinum

Yukimi Jyoko*, Ryuji Koyama* and Yasunori Hayashi*

Monatomic steps on Pt single crystal surfaces have been directly imaged in a conventional electron microscope in reflection mode. With the reflection electron microscopy (REM) technique the surface topography of Pt single crystal spheres at the progressive stages of Cu electrocrystallization has been studied. Although the formation of Cu sub-monolayer superstructures on Pt(111) surfaces has not yet been detected, a layered Cu deposition of one monolayer or two and the Stranski-Krastanov type crystal growth, which is influenced by the surface steps, have been observed. Deposition of bulk Cu and subsequent stripping altered the Pt(111) surface, leaving traces of the Cu deposit geometry on the bare Pt surface after removal of Cu by anodic stripping. No such a surface change was visible during Cu adsorption-desorption cycles only in the underpotential region. The observed REM images have been discussed in terms of surface rearrangements during Cu electrocrystallization due to the formation of layered deposition and bulky island crystals.

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I. Introduction

The real space imaging of surface topography on atomic scale is of great interest in surface science and technology. Reflection electron microscopy (REM) is capable of resolving monatomic height steps on single crystal surfaces⁽¹⁾⁻⁽⁴⁾. In combination with electron diffraction crystallographic information on the surface can also be obtained. Structures and growth behavior of metal adlayers, which constitute the first step for deposition of thin metal films, have been investigated thoroughly for gas-phase deposition. The situation is quite different for the technically important and widely used electrochemical deposition from aqueous solutions. The atomic arrangement of adlayers on electrode surfaces could only be studied by electron diffraction methods after the emersion of the electrode from the solutions and subsequent transfer into a vacuum chamber⁽⁵⁾⁽⁶⁾. Recently, *in situ* scanning tunneling microscope (STM) images have revealed the surface atomic arrangements⁽⁷⁾⁻⁽¹⁰⁾. We here present the results of an REM study which allows the atomic scale observation in real space for the initial stages of Cu electrocrystallization on Pt single crystal surfaces controlling the electrode potential from the standpoint of well-defined film preparation.

II. Experimental

Single crystal Pt spheres were prepared by melting one end of a Pt wire of 0.2 mm diameter in a hydrogen-oxygen flame, the resulting Pt droplet then being allowed to solidify to a spherical crystal of 0.3–0.5 mm diameter as described by Clavilier *et al.*⁽¹¹⁾. The shadow image of the crystal sphere is shown in Fig. 1. The flat area on the

sphere is a (111) facet. Such a specimen is suitable for both electrochemical and electron microscopic investigations. The REM imaging of the (111) faces was achieved near the $[1\bar{1}0]$ azimuth at the orientation where the Bragg reflection shows an intensity enhancement. This enhancement is a surface channeling effect which depends on the azimuth and the quality of the surface⁽²⁾. Image intensity and contrast of the surface structure were significantly increased using such a reflection.

The electrochemical experiments were performed in a standard type electrochemical cell with separated compartments for the reference and the Pt counter electrodes to control the potential of the Pt sphere working electrode. All the electrode potentials were measured and quoted with respect to the silver-silver chloride electrode (Ag/AgCl). The electrolyte, 0.5 mol/L H_2SO_4 containing 3×10^{-4} mol/L $CuSO_4$ was prepared with analytical grade reagents and distilled water and deoxygenated with purified nitrogen. Unless otherwise indicated, all the measurements were performed in an atmosphere of purified nitrogen at ambient temperature. Before each electrochemical experiment the Pt spheres

Fig. 1 Electron shadow image of Pt single crystal sphere.

* Faculty of Engineering, Kyushu University, Fukuoka 812, Japan.

Fig. 2 Anodic current-potential curves: $\cdots$, for a Pt single crystal sphere electrode in 0.5 mol/L H_2SO_4 ; $-\cdot-$, 0.6 monolayer (ML) Cu-covered Pt electrode in 0.5 mol/L H_2SO_4 containing 3×10^{-4} mol/L CuSO_4 ; $—$, 1.8 ML Cu-covered Pt electrode; and $- - -$, 4.2 ML Cu-covered Pt electrode, recorded at a scan rate of 0.5 V/s. The current peak 1 corresponds to the dissolution of Cu adlayer on Pt and peak 2 corresponds to that of Cu deposits on Cu adlayer.

were heated in a gas flame up to about 1800 K for several minutes and subsequently cooled down in air. This flame treatment has proved to be an efficient cleaning procedure for the electrode which yields reproducible current-potential curves⁽¹⁰⁾. A typical anodic current-potential curve for such a Pt single crystal sphere in 0.5

mol/L H_2SO_4 is shown in Fig. 2 (indicated by a dotted curve). This current-potential curve is identical with that of an ordinary polycrystalline Pt electrode.

III. Results and Discussion

The initial stages of electrochemical metal deposition often occur at potentials positive to the reversible Nernst potential, E_r for the corresponding bulk metal deposition⁽¹²⁾. This so-called underpotential deposition of the first monolayer onto a foreign metal substrate reflects the fact that the adatom-substrate bond is stronger than adatom-adatom bond. This phenomenon has been studied mainly by cyclic voltammetry, which led to a detailed thermodynamic description of the adlayer. Figure 2 shows anodic stripping current-potential curves for Pt single crystal sphere electrodes with various coverages of Cu electrodeposited under potential control in 0.5 mol/L H_2SO_4 containing 3×10^{-4} mol/L CuSO_4 ($E_r = 0.035$ V vs. Ag/AgCl), recorded at a scan rate of 0.5 V/s. The dissolution current peaks for Cu deposited on the Pt single crystal sphere electrode are numbered. The electrode potential is a direct measure of the free energy of adsorption; therefore, current integration yields the adsorption/desorption isotherm. From the difference in potential for the current peak due to desorption of the first monolayer of Cu deposited in the underpotential region (peak No. 1 in Fig. 2) and that due to bulk Cu dissolution (peak No. 2 in Fig. 2), an excess binding energy of approximately 7.7×10^4 J/mol (0.8 eV) is deduced for the Cu adatoms on the Pt electrode.

Fig. 3 REM image and corresponding RHEED pattern of a (111) facet of a Pt single crystal sphere with monatomic steps and a screw dislocation emerging through the surface using intensity enhanced (444) Bragg reflection near the $[1\bar{1}0]$ azimuth at 80 kV.

Moreover, a coverage evaluation from the charge connected with the dissolution peaks yields Cu coverages of 0.60, 1.8, and 4.2 monolayers for the Pt electrodes, respectively, indicated by a dash-dot-dash curve, a solid curve, and a broken curve in Fig. 2.

In Fig. 3 the reflection electron diffraction (RHEED) pattern from the (111) surface of a freshly prepared Pt single crystal sphere is shown together with the REM image recorded with the strongly excited Bragg reflection. The Bragg reflections are elongated into streaks perpendicular to the shadow edge indicating a smooth crystal surface. The small angle between imaging beam and specimen surface causes a severe foreshortening and hence a reduction of resolution in the direction of observation, as indicated by the two magnification bars. In order to reduce the foreshortening effect a higher order, the (444) Bragg reflection is used for imaging. The contour lines seen in the REM picture are monatomic steps; between these lines the surface is atomically flat. An analysis of the image contrast allows the sense of the steps to be determined⁽¹³⁾⁽¹⁴⁾. The image is in focus only in a very narrow horizontal area with minimum contrast of

surface details, while above this area the image is in over-focus and below it in underfocus. Between the atomic steps, small loops are visible which are atomic height protrusions or depressions. A screw dislocation emerging through the surface can also be seen, as indicated by the arrow. The same REM image was observed for the (111) surface of the Pt sphere subjected to a few potential scans in the Cu^{2+} ion-free base electrolyte, and even in the Cu^{2+} ion containing electrolyte, provided that Cu deposition was carefully avoided during the potential cycling.

Figure 4 shows REM images and corresponding RHEED patterns of the (111) surfaces of Pt single crystal spheres covered with electrochemically deposited Cu. The REM images were recorded near the $[\bar{1}\bar{1}0]$ azimuth with the intensity enhanced (444) Bragg reflection. The REM image shows clear surface steps when covered with submonolayer of Cu and flat deposits at some two monolayer coverage (Fig. 4(a) and Fig. 4(b)). The atomic structure of an ordered Cu adlayer on the Au(111) electrode surface, a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ superstructure which indicated repulsive interactions between closely spaced

Fig. 4 REM images and corresponding RHEED patterns of Cu-covered Pt(111) surfaces.

Cu adatoms, was resolved by LEED or RHEED investigations⁽⁵⁾⁽⁶⁾ and in STM images⁽¹⁰⁾. This structure differed from the pseudomorphic Cu adlayer formed under vacuum conditions⁽⁵⁾, which demonstrated the structure-determining role of coadsorbed anions in the electrolyte⁽⁶⁾⁽¹⁰⁾. In our RHEED patterns, however, no such Cu submonolayer superstructure on the Pt(111) surface has yet been detectable. With an increase in coverage, disk-shaped crystals which are markedly influenced by the surface steps are observed in the REM image. The RHEED pattern from the Pt(111) surface covered with several monolayers of Cu shows the additional spots due to an epitaxial growth of island Cu crystals besides the fun-

damental diffraction streaks (Fig. 4(c)). These observations demonstrate a layer-by-layer crystal growth up to one or two monolayers and an epitaxial island growth on top of the deposited layer influenced by the surface steps for the further growth. This is apparently quite different from the usual growth of three-dimensional particles. The growth process of the observed electrocrystallization, therefore, may be a particular case of the Stranski-Krastanov mode.

REM experiments also revealed that Cu adsorption-desorption cycles only in the underpotential region left the surface topography of Pt single crystals unchanged. Deposition of bulky island of Cu at potentials negative

Fig. 5 REM images of a partially electrodeposited specimen: (a) the lower half of the image is some ten monolayers of Cu by repetitive Cu deposition and stripping under cyclic potential control; (b) the image of the same area as (a) after stripping of all deposited Cu by anodic polarization.

to E_r and subsequent stripping at a potential positive enough to guarantee a Cu-free surface, however, altered the Pt(111) surface. In Fig. 5 REM images of a Pt(111) surface partially covered with (a) and without (b) some ten monolayers of Cu by repetitive Cu deposition and stripping under cyclic potential control are shown together with the corresponding RHEED patterns. This surface change is obviously seen in the REM image, of which the upper half possesses the clean Pt(111) surface escaping any Cu deposition, as traces of the Cu deposit geometry left on the bare Pt surface after removal. (Compare Fig. 5(b) with Fig. 5(a).) A tentative explanation of this observation is as follows: Bulk Cu deposition immediately leads to alloying, and dissolution of Cu leaves a rearranged surface with small, randomly oriented Pt crystals, which demonstrates a more complicated deposition process. Further experiments are necessary to confirm this finding.

In summary, we have presented REM images of the early stages of Cu electrocrystallization on Pt(111) surfaces under the electrode potential control, which reveal the presence of the layered Cu deposition of one monolayer or two and the Stranski-Krastanov type crystal growth significantly influenced by the surface steps.

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