Preparation of Cobalt/Platinum Multilayers by Electrocrystallization

Yukimi Jyoko, Satoshi Kashiwabara and Yasunori Hayashi

Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

Electrocrystallization of atomically controlled metallic multilayers has been discussed on the basis of a nucleation-growth mechanism and experimental observations. Monatomic steps on Pt single crystal surfaces have been directly imaged using a conventional transmission electron microscope in the reflection mode. With this reflection electron microscopy (REM) technique, the initial stages of Co electrocrystallization on Pt(111) surfaces have been studied under potential control. The REM images have revealed a layer by layer growth, strictly speaking, a simultaneous multinuclear multilayer growth of Co deposition in the range from submonolayer coverage up to some ten monolayers. Based on the observations of the surface morphology and the reflection electron diffraction from an REM study, the feasibility of electrocrystallization to produce Co/Pt multilayers with a comparable structure to those prepared by vapor-phase deposition techniques is discussed.

(Received August 5, 1992)

Keywords: electrocrystallization, reflection electron microscopy, layer by layer growth, cobalt/platinum multilayer, metallic artificial superlattice

I. Introduction

Metallic artificial superlattices, which are of great interest for their unusual and sometimes outstanding magnetic, electrical and mechanical properties which are principally caused by the existence of interfaces and layered structure, have been the subject of intensive studies. The overwhelming majority of these metallic multilayer films have been produced by vacuum deposition, molecular beam epitaxy (MBE) or sputtering which are suitable for the controlled preparation of individual layers on the order of monatomic layers. Electrocrystallization from aqueous solutions may also be a promising candidate for this purpose. It must be emphasized that the electrocrystallization process is more suitable for producing metallic multilayers of a large area in an arbitrary shape than the vapor-phase deposition techniques, and that it can be carried out at room temperature. This may be important for systems in which undesirable interdiffusion between the adjacent layers may readily occur. We have focused our attention on the capability of electrocrystallization to produce metallic multilayers with predesignable, variable, and controllable composition and structure on an atomic scale. Very few papers directly concerning this subject, however, have been published so far.

In the last decade, the use of an electron microscope for surface imaging in the reflection mode has shown a considerable potential for studying crystal surfaces. The technique of reflection electron microscopy (REM), which can provide crystallographic information on the surface and easily reveal fine detail such as monatomic height steps, surface domains with different chemical compositions, and surface dynamic processes of the single crystal, has become one of the most important

microscopic methods for investigating surface atomic structures, as recently reviewed by Cowley⁽¹⁾ and Yagi⁽²⁾. We have previously reported REM observations for the initial stages of Cu electrocrystallization on Pt single crystal surfaces controlling the electrode overpotential, which corresponds to the supersaturation in gas-phase depositions, from the standpoint of well-defined film preparation⁽³⁾. On the other hand, *in situ* scanning tunneling microscope (STM) or atomic force microscope (AFM) images have recently revealed the atomic structure of metal adlayers on electrode surfaces⁽⁴⁾⁽⁵⁾. The structure differed from the pseudomorphic structure observed for gas-phase deposition, which demonstrated the energetic and structural effects of coadsorbed anions in the electrolyte. In this paper we present the results of an REM study of Co electrocrystallization on Pt(111) surfaces under potential control as part of an effort directed toward the preparation of atomically controlled Co/Pt multilayers by electrocrystallization.

II. Kinetics of Nucleation and Growth in Electrocrystallization

A solidification process proceeds *via* nucleation of crystal nuclei together with their subsequent growth under a significant degree of supersaturation. The theory of nucleation and growth in metal electrocrystallization has been well developed during the last two decades⁽⁶⁾⁽⁷⁾. The nucleation frequency J increases with an increase in crystallization overpotential η , according to the two-dimensional nucleation mechanism, as expressed in the following equation.

$$J = K_1 \exp(\eta/K_2) \quad (1)$$

where K_1 and K_2 denote constants. The kinetics of formation of one monatomic layer on an intact face is deter-

mined both by the two-dimensional nucleation frequency J [nuclei·m⁻²·s⁻¹] and the propagation rate of the monatomic steps v [m·s⁻¹] in the polynuclear growth mechanism, and is given⁽⁸⁾⁻⁽¹⁰⁾ by

$$i = q_{\text{mon}} b J v^2 t^2 \exp(-b J v^2 t^3 / 3) \quad (2)$$

where q_{mon} is the electric charge needed for forming a unit area of one monolayer and b is a geometrical factor. In this equation, the preexponential term indicates the current flowing to the peripheries of the independently growing nuclei which are progressively formed with time. The exponential term takes into account the overlapping of the growing nuclei in terms of the Kolmogorov-Avrami formulation⁽¹¹⁾⁽¹²⁾. In an early stage, before overlapping has occurred, the current follows the quadratic relation required by the preexponential term, and from the slopes of a series of i vs. t^2 plots recorded at different overpotentials, the value of Jv^2 as a function of η can be obtained. The propagation rate v has been found to be of the order of 10⁻² m·s⁻¹ and slightly dependent on the overpotential η ⁽¹³⁾⁽¹⁴⁾. Equation (2) gives the kinetics of the monolayer formation. As nucleation proceeds continuously, however, new nuclei are formed on top of the deposited first layer long before it has covered the whole area of the face. The same happens with the third layer, fourth and so on as soon as their extensions become large enough to make the nucleation possible. The deposition process under such conditions is known as multinuclear multilayer growth, and theoretically up to seven layer levels of nucleation and propagation are expected to simultaneously proceed. This mechanism has been theoretically analyzed⁽¹⁵⁾⁻⁽¹⁷⁾ based on the Kolmogorov-Avrami theory or using the Monte Carlo simulation technique⁽¹⁸⁾. The theoretical calculations have shown that after an initial rise according to the preexponential term of eq. (2), the transient current passes through several oscillations at relatively low overpotentials and tends to a steady final value i_{∞} . This steady state current density is given by

$$i_{\infty} = q_{\text{mon}} \beta (b J v^2)^{1/3} \quad (3)$$

where β is a dimensionless constant varying around unity from theory to theory. Thus, the growth process in electrocrystallization is characterized by an initial rise in current under potentiostatic condition, depending on crystallization overpotential. Such oscillations of the potentiostatic transient current are very similar to the intensity oscillations in the reflection high energy electron diffraction (RHEED) during MBE growth.

III. Experimental

Single crystalline Pt spheres were prepared as described in the previous paper⁽³⁾. The REM image of the (111) faces on the Pt spheres was recorded with a specular Bragg reflection condition fulfilled for an 80 kV incident electron beam in a direction close to the [121] or [110] zone axis, with a glancing angle of one or two degrees. The small angle between imaging beam and

specimen surface causes a severe foreshortening of the image and hence a reduction in resolution in the direction of observation. To reduce the severe foreshortening, a relatively high order Bragg reflection was used for imaging. In order to increase image intensity and contrast of the surface structure, the surface resonance condition was used to enhance the Bragg reflection for image formation. This surface resonance condition has been considered to be associated with the simultaneously diffracted beams travelling in the directions parallel or nearly parallel to the crystal surface. It has been suggested that under the resonance condition, the intensity enhancement of the specular Bragg-reflected beam observed in the RHEED pattern is due to an increase in both elastic and inelastic electron scattering⁽¹⁹⁾. The surface REM image obtained from the resonance condition in this study showed a better topographical image contrast for the surface structure.

The electrochemical experiments were done in a standard type three-electrode electrolytic 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 saturated silver-silver chloride electrode (Ag/AgCl). The electrolyte, 0.5 mol/L H₂SO₄ containing 0.1 mol/L CoSO₄, was prepared with analytical grade reagents and distilled water, and was deoxygenated with bubbling purified nitrogen gas. Unless otherwise indicated, all measurements were made in an atmosphere of purified nitrogen at ambient temperature. Prior to each electrochemical experiment, the Pt sphere was flame annealed. This flame treatment has proved to produce flat crystal surfaces and to be an efficient cleaning procedure for the electrode which yields reproducible current-potential curves⁽³⁾. A typical anodic current-potential curve for such a Pt single crystal sphere in 0.5 mol/L H₂SO₄ solution is shown in Fig. 1 (indicated by the dotted curve). This polarization curve is identical with that of an ordinary polycrystalline Pt electrode.

IV. Results and Discussion

The initial stages of metal electrocrystallization often occur at potentials positive to the reversible Nernst potential $E_r (= E_0 + (2.3RT/zF) \log [M^{z+}])$ for corresponding bulk metal deposition⁽²⁰⁾. 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 the adatom-adatom bond. This phenomenon has been studied mainly by cyclic voltammetry, which led to a detailed thermodynamic description of the adlayer. Figure 1 shows anodic stripping current-potential curves for Pt single crystal sphere electrodes with various coverages of Co, a relatively less noble metal, electrodeposited in the range from sub-monolayer coverage (Fig. 1(a)) to several monolayers (Fig. 1(b)) under potential control in 0.5 mol/L H₂SO₄ solution containing 0.1 mol/L CoSO₄ ($E_r = -0.5$ V vs.

Fig. 1 Anodic stripping current-potential curves for Pt single crystal sphere electrodes with various coverages of electrodeposited Co in 0.5 mol/L H_2SO_4 solution containing 0.1 mol/L CoSO_4 recorded at a scan rate of 0.5 V/s; (a) —, 0.3 monolayer Co-covered Pt electrode, — · — ·, 0.9 monolayer Co-covered Pt electrode, and (b) —, 1.8 monolayer Co-covered Pt electrode. Dotted curves in (a) and (b) show the reference curve for the Pt substrate.

Ag/AgCl), recorded at a scan rate of 0.5 V/s. The dissolution current peaks for Co deposited on the Pt sphere electrode are numbered. Current peak 1 corresponds to the dissolution of the first monolayer of Co deposited on the Pt sphere in the underpotential region, and peak 2 corresponds to that of Co deposits on the Co adlayer. 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 peaks of 1 and 2, an excess binding energy of approximately 1.4×10^5 J/mol (1.4 eV) is deduced for the Co adatoms on Pt with reference to Co on Co adatoms. Moreover, the evaluation of the Co coverage from the electric charge connected with the dissolution peaks yields the coverages of 0.3, 0.9, and 1.8 monolayers for the Pt electrodes, respectively, indicated by a solid curve, a dash-dot-dash curve in Fig. 1(a), and a solid curve in Fig. 1(b).

Figure 2 shows a typical potentiostatic transient current for Co electrocrystallization on a Pt single crystal sphere electrode recorded at a relatively high overpotential of -0.8 V (vs. Ag/AgCl) in the 0.5 mol/L H_2SO_4 solution containing 0.1 mol/L CoSO_4 . The experimental

Fig. 2 A typical potentiostatic transient current for Co electrocrystallization on a Pt single crystal sphere electrode recorded at -0.8 V (vs. Ag/AgCl) in 0.5 mol/L H_2SO_4 solution containing 0.1 mol/L CoSO_4 .

transient current exhibits an initial rise in current which is characteristic of the nuclear growth process as described in Section II. The initial parts of the transient current follow the quadratic law given by the preexponential term of eq. (2). In the further course, the transient shows the first maximum for the formation of the first monatomic layer, however, followed by only a small current oscillation in comparison with the theoretical transients^{(15)–(18)} calculated for the layer by layer growth mechanism. One possible explanation for this time dependence of the current is that the nucleation proceeds on a limited number of active sites on the surface, or at a higher nucleation rate in the beginning of the deposition, and that by the simultaneous multilayer growth, a complicated multilevel structure is created on the crystal face.

In Fig. 3(a) the RHEED pattern obtained from the (111) surface of a freshly prepared Pt single crystal sphere is shown together with the REM image recorded with the strongly excited (444) specular Bragg reflection near the $[1\bar{2}1]$ azimuth. The Bragg reflections are elongated into streaks perpendicular to the shadow edge indicating an atomically smooth crystal surface. Although the image suffers foreshortening in the beam direction, as indicated by the two magnification bars, the resolution obtained in the lateral direction is better than one nanometer. Several contrast-producing mechanisms can be involved, giving sensitivity to the micromorphology of the surface. The contour lines seen in the REM picture are monatomic height steps, and between these lines the surface is atomically flat. An analysis of the image contrast allows the sense of the steps to be determined⁽²¹⁾⁽²²⁾. The same REM image was observed for the (111) surface of the Pt sphere subjected to a few potential scans in the Co^{2+} -free base electrolyte, and also in the Co^{2+} containing electrolyte, provided that Co deposition was carefully avoided after the potential cycling.

The REM image of the (111) surface of the Pt sphere

Fig. 3 REM images and corresponding RHEED patterns; (a) obtained from a (111) facet of a Pt single crystal sphere with monatomic steps, and (b) the (111) surface of the Pt sphere covered with an electrochemically deposited 0.3 monolayer Co, recorded with the strongly excited (444) specular Bragg reflection near the $[1\bar{2}1]$ azimuth under a surface resonance condition fulfilled for an 80 kV incident electron beam.

covered with an electrochemically deposited to sub-monolayer is shown together with the corresponding RHEED pattern in Fig. 3(b). The REM image shows clear surface steps and no remarkable change in the surface topography of the Pt single crystal is seen for Co sub-monolayer coverage, except for only a slight alteration in the flat terraces. In the RHEED pattern, such a Co sub-monolayer superstructure on the Pt(111) surface has not been detected as a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure observed for Cu on Au(111) in *in situ* STM or AFM images⁽⁴⁾⁽⁵⁾, which demonstrated the structure-determining role of coadsorbed anions in the electrolyte.

Figure 4 shows REM images and corresponding RHEED patterns obtained from the (111) surfaces of Pt single crystal spheres with various coverages of electrodeposited Co. The REM images were recorded with the intensity enhanced (444) specular Bragg reflection near the $[1\bar{1}0]$ azimuth. The REM picture shows an epitaxial and multinuclear monolayer deposition when covered with one or two monolayers of Co (Fig. 4(a)). With an increase in coverage, new two-dimensional nuclei are formed on top of the previously deposited monatomic layer long before it has covered the entire surface. Such an epitaxial and simultaneous multilayer growth is observed for Co electrocrystallization in the

range from several monolayer coverages up to some ten monolayers (Fig. 4(b) and Fig. 4(c)). This growth process is apparently quite different from the Stranski-Krastanov type growth observed for Cu electrocrystallization⁽³⁾ which is an epitaxial and three-dimensional island growth influenced by the surface steps on top of the layered deposition of one or two monolayers. This is a modification of the Frank-van der Merwe (FM) mode, which has also been called the pseudo-FM mode⁽²³⁾⁽²⁴⁾.

REM experiments have also revealed the capability of preparing atomically controlled Co/Pt multilayers by electrocrystallization. In Fig. 5, a representative REM image of a double layer specimen is shown together with the corresponding RHEED pattern. The film is composed of several monolayers of Co on a Pt(111) substrate and several monolayers of Pt further electrodeposited on Co under potential control. A pair of RHEED patterns was obtained from the specimen for an incident electron beam in a direction close to the $[1\bar{1}0]$ zone axis with a large incidence angle (Fig. 5(a)) and a small incidence angle (Fig. 5(b)). The REM image was recorded with the intensity enhanced (555) specular Bragg reflection near the $[1\bar{1}0]$ azimuth. In the REM picture, a relatively good epitaxial homogenous layered structure is observed. The RHEED patterns also show additional spots besides the

Fig. 4 A series of REM images and corresponding RHEED patterns obtained from Pt(111) surfaces with various coverages of electrodeposited Co; (a) 1.8 monolayer Co-covered, (b) 4.1 monolayer Co-covered, and (c) 8.2 monolayer Co-covered, recorded with the intensity enhanced (444) specular Bragg reflection near the $[1\bar{1}0]$ azimuth.

fundamental diffraction streaks, which could probably be assigned to the formation of ordered domains of a CoPt_3 alloy at the interface between the adjacent deposited layers. A tentative explanation of these observations is as follows: Bulk deposition immediately leads to alloying, which indicates a more complicated deposition process for the monolayer. Presumably a sur-

face rearrangement occurs during electrocrystallization, which would also explain the high kinetic barrier often found in underpotential deposition.

Further progress in the various experimental techniques is necessary in order to achieve improved quality of electrodeposited metallic multilayers regarding the coherence and the uniformity of the layered structure,

Fig. 5 A typical REM image and corresponding RHEED pattern of a double layer specimen, several monolayers of electrodeposited Pt/4.1 monolayer Co/Pt(111), recorded with the intensity enhanced (555) specular Bragg reflection near the $[1\bar{1}0]$ azimuth. A pair of RHEED patterns obtained from the specimen for an incident electron beam in a direction close to $[1\bar{1}0]$ zone axis with (a) a large and (b) a small incidence angle.

which is comparable or superior to those produced by vapor-phase deposition. Electrocrystallization under precise overpotential control, however, has the potential of allowing the creation of multilayered structures with a high degree of homogeneity and epitaxial coherency, or metallic artificial superlattices exhibiting unusual properties previously unavailable by conventional preparation techniques.

In summary, we have presented REM images of the early stages of Co electrocrystallization on Pt(111) surfaces under potential control, which have revealed the presence of a simultaneous multilayer growth in the range from submonolayer coverage up to some ten monolayers. And that demonstrates the feasibility of the preparation of electrodeposited Co/Pt multilayers with an epitaxial homogenous layered structure extending over several monolayers.

Acknowledgement

This study was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas 'Metallic Artificial Superlattice' from the Ministry of Education, Science and Culture.

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