Temperature Dependence of Inward Diffusion of Underpotentially-Deposited Cd into a Au (100) Bulk Phase under Electrochemical Environment*¹

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We investigated the inward diffusion of underpotentially-deposited (UPD) Cd into a Au (100) substrate in 50 mol m⁻³ sulfuric acid solution under potential control by anodic voltammetry at the temperature range from 295 to 333 K, as well as by the electrochemical quartz crystal microbalance (EQCM) analysis and X-ray diffractometry (XRD). The anodic voltammograms show that inward diffusion of the Cd adatoms into a Au (100) bulk phase is classified into two types of steps. One is a very fast step, which is the diffusion of UPD Cd into a Au (100) electrode at the surface layer; the activation energy of this step is $\cong 70 \text{ kJ mol}^{-1}$. The other is a much slower step; the activation energy of this step (110 kJ mol^{-1}) agrees well with that of Cd bulk diffusion into a Au–Cd compound. The amount of UPD Cd is calculated from EQCM analysis, and it nearly agrees with that obtained from anodic voltammetry. We found that the amount of UPD Cd increases with temperature. We confirmed the formation of β Au–Cd layer on the sample by XRD after maintained at the UPD region of -1100 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ for 1 h at 333 K.

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1. Introduction

At a metal surface in contact with electrolyte under an influence of electric field, the strong interaction between the underpotentially-deposited (UPD) adatom and the topmost bulk atom cause the intermixing at the interface under the UPD regions as for Pb,^{1–6} Ti^{5,7} and Cd^{8,9} on Ag, Pb,⁶ Ag,^{10,11} Cu,¹² Te¹³ and Cd¹⁴ on Au, Hg,¹⁵ Cu¹⁶ and Ag^{17,18} on Pt, and Sn¹⁹ on Cu. These works suggest that surface alloy formation is a common phenomenon for such UPD systems characterized by a strong adatom-substrate interaction. However, inward diffusion at a metal/electrolyte interface is poorly understood.

The surface alloying of UPD Cd and a Au substrate has been the subject of several studies.^{20–23} We reported on the stripping of Cd from the surface alloyed layer on a Au (100) substrate by the electrochemical atomic force microscope (EC-AFM).^{20–22} We found by anodic voltammetry that the thickness of the UPD Cd layer was not limited to 1 monolayer (ML) but increased with holding time. And then, we proposed a new model for the surface alloy formation in Cd on Au system. The model was confirmed in studies of Inzelt and Horányi²³ by electrochemical quartz crystal microbalance (EQCM) analysis.

In this study, we investigated the temperature dependence of inward Cd diffusion by anodic voltammetry. Then, the amount of UPD Cd calculated from the EQCM analysis was compared with that obtained from the anodic voltammetry. Finally, we revealed by X-ray diffractometry (XRD) the structure formed on the Au (100) substrate after the long-term holding at a potential of -1100 mV .

2. Experimental

2.1 Anodic voltammetry

The working electrode used was a Au (100) single crystal, which were prepared from a single-crystal Au rod (disk, 12 mm diameter) grown by the Bridgman method. The sample preparation of Au (100) was almost the same as that reported previously.^{24,25} The counter electrode was an Au wire and the reference electrode a $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode, to which all potentials are referred. The electrolyte solutions used in anodic voltammetry were prepared from H_2SO_4 (Wako Chemical, ultrapure), CdSO_4 (Rare metallic, 99.999%) and ultrapure water (Millipore Simpli Lab, $\cong 18.2 \text{ M}\Omega\text{cm}$). The experiments were conducted in 50 mol m⁻³ H_2SO_4 + 1 mol m⁻³ CdSO_4 solution, deoxygenated with argon gas for 2 h prior to use. The Nernst potential of the Cd bulk deposition in this solution ($E_{\text{Cd}/\text{Cd}^{2+}}$) at room temperature (RT) is -1143 mV . The experiments were performed at 295 (RT), 303, 313, 323 and 333 K.

2.2 EQCM analysis

EQCM analysis at RT was performed for comparison with the anodic voltammetry. The working electrode was a Au polycrystal on quartz crystals of 6 MHz (geometrical area, $A = 1.457 \text{ cm}^2$). Other conditions were the same as those in anodic voltammetry. The Sauerbrey equation ($\Delta F = -C_f \times \Delta W$), where the integral sensitivity of the crystal (C_f) is equal to $8.14 \times 10^7 \text{ Hz cm}^2 \text{ g}^{-1}$, was applied to calculate the mass change, ΔW from the frequency shift, ΔF .

2.3 XRD

Low-angle XRD (0.5 deg.) were performed in order to analyze the structure formed on the Au (100) surface after 1 h holding under -1100 mV at 333 K. XRD was operated at the condition of 40 kV, 200 mA, for $\text{CuK}\alpha$, using a Rint 2500 X-ray powder diffractometer.

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Fig. 1 Cyclic voltammogram of a Au (100) in 50 mol m⁻³ H₂SO₄ + 1 mol m⁻³ CdSO₄ solution at RT. Sweep rate: 50 mV s⁻¹. The atomic structures of UPD Cd adlayers as observed by EC-AFM at the potentials shown by arrows.

3. Results and Discussion

3.1 Anodic voltammetry

The inward diffusion of UPD Cd into a Au (100) electrode was studied in 50 mol m⁻³ H₂SO₄ + 1 mol m⁻³ CdSO₄ solution at RT (295 K). The cyclic voltammogram (CV) of the electrode is shown in Fig. 1. This result agrees well with those of previous reports.^{20–22)} We have previously found that the amount of UPD Cd on a Au (100) electrode is about 1 ML of (1 × 1) Cd, after 1 min maintained at -1000 mV in the UPD region, and it does not increase significantly with increase in holding time. Therefore we maintained the potential of -1000 mV for more than 1 min in order to cover the entire Au (100) surface with UPD Cd adatoms before every experiment. Then, the potential was stepped instantaneously from -1000 to -1100 mV, which is also the UPD region. After holding at -1100 mV for different times (1–1800 s), the potential was swept back to 0 mV at a sweep rate of 50 mV s⁻¹. The anodic voltammograms from -1100 to 0 mV were shown in Fig. 2. Anodic current in the Fig. 2 corresponds to the dissolution rate of UPD Cd. Figure 3 shows the total charge calculated by integration of anodic current in Fig. 2 against holding time at -1100 mV. In Fig. 3, the right ordinate, θ is calculated from the total charge, where the charge is 381 $\mu\text{C cm}^{-2}$ for 1 ML of Cd atoms on the assumption of Faraday's law. It was found that the charge associated rapidly over 1 ML and increased continuously with increase in holding time at -1100 mV, although Cd bulk phase deposition did not occur. Therefore, it is considered that UPD Cd adatoms diffused inwardly into the Au (100) bulk phase. Then, assuming that the diffusion of Cd atoms is governed by Fick's law, we considered the following equation because of constant surface concentration:

$$Y = (q - q_0)\pi^{1/2}/4Fc_0 = (D \cdot t)^{1/2} \quad (1)$$

where q is the total charge, q_0 the charge of UPD Cd at -1000 mV for 1 min ($\cong$ the amount of (1 × 1) Cd on a Au

(100)), F the Faraday's constant, D the diffusion coefficient and c_0 the surface concentration, which corresponds to 0.00688 mol cm⁻². Figure 4 shows the relationship between the diffusion depth, Y and the holding time, $t^{1/2}$, indicating that diffusion coefficient ($D^{1/2}$) changes with holding time ($t^{1/2}$). From the anodic voltammetry, it is suggested that the overall diffusion consists of two steps. One is a very fast step represented by D_1 , in which UPD Cd adatoms diffuse into a Au (100) bulk phase at the surface layer (turnover process). The other is much slower step represented by D_2 , which is governed by the bulk diffusion step.

3.2 EQCM analysis

The amount of UPD Cd is also studied by the EQCM analysis, which is compared with that obtained from the anodic voltammetry. The working electrode used in both experiments is the same Au polycrystalline substrate. For both experiments, after the potential was maintained for 10 min at -1000 mV for full coverage of the UPD Cd adatoms on a Au (100), the potential was instantaneously stepped from -1000 to -1100 mV and maintained at -1100 mV for different times (1–1800 s). The total quantities of the UPD Cd calculated from the EQCM analysis are plotted in Fig. 5, in comparison with the total charge obtained from the anodic voltammetry. As seen in Fig. 5, both data were almost in agreement. This means that the amount of UPD Cd adatoms can be determined from the total charge obtained from anodic voltammograms.

3.3 Anodic voltammetry at increasing temperature

Anodic voltammetry were also performed at 303, 313, 323 and 333 K. The experimental procedure and the determination of D_1 and D_2 are the same as these performed at RT (295 K). Figure 6 shows the Arrhenius plots for D_1 and D_2 . Generally, diffusion coefficient D_i ($i = 1, 2$) can be written as

$$D_i = D_{i0} \exp(-Q_i/RT) \quad (2)$$

as a function of temperature T by the activation energy Q_i of diffusion.

Figure 6 shows that the activation energies Q_1 and Q_2 are 70 kJ mol⁻¹ and 110 kJ mol⁻¹ calculated by eq. (2), respectively. The Q_2 is in good agreement with that for the bulk diffusion of Cd into a Au–Cd compound ($= 113 \text{ kJ mol}^{-1}$).²⁶⁾ Thus, it may be strongly expected that step 2 is governed by the bulk diffusion. On the other hand, the smaller Q_1 than the Q_2 , suggests that step 1 may corresponds to be diffusion in the thin surface layer.

The anodic voltammograms at 333 K are shown in Fig. 7. As shown in the Fig. 7, the new peak (d_3) is appeared and that current density increases particularly in comparison with that at RT with increase in holding time $t > 240$ s. We also found that the color of Au (100) surface changed to silver white after maintaining the potential at -1100 mV for more than 240 s.

The sample after 1 h holding under -1100 mV at 333 K was inspected by low-angle XRD (Fig. 8). In the X-ray diffraction patterns in Fig. 8, no Cd peaks were observed while only β Au–Cd alloy peaks were observed, indicating that the β Au–Cd is formed on the substrate surface.

Fig. 2 Anodic voltammograms obtained after different holding times at -1100 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ at RT. Systems: $\text{Au (100)}/50 \text{ mol m}^{-3} \text{ H}_2\text{SO}_4 + 1 \text{ mol m}^{-3} \text{ CdSO}_4$. Sweep rate: 50 mV s^{-1} .

Fig. 3 Time dependence of total charge during anodic voltammetry after holding at -1100 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ for different times at RT. The ordinate on the right side is the thickness of UPD Cd layer, where the amount of (1×1) Cd on Au (100) is 1 ML. System: $\text{Au (100)}/50 \text{ mol m}^{-3} \text{ H}_2\text{SO}_4 + 1 \text{ mol m}^{-3} \text{ CdSO}_4$.

Fig. 4 Time dependence of diffusion depth, Y after holding at -1100 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ for different times at RT. System: $\text{Au (100)}/50 \text{ mol m}^{-3} \text{ H}_2\text{SO}_4 + 1 \text{ mol m}^{-3} \text{ CdSO}_4$.

Fig. 5 Amount of UPD Cd atoms obtained from EQCM analysis and anodic voltammetry when the potential is maintained at -1100 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ for different times at RT. System: $\text{Au polycrystal}/50 \text{ mol m}^{-3} \text{ H}_2\text{SO}_4 + 1 \text{ mol m}^{-3} \text{ CdSO}_4$.

Fig. 6 Arrhenius plots of the diffusion coefficients D_1 and D_2 for Cd diffusion into a Au (100) electrode at different temperatures (295, 303, 313, 323 and 333 K). System: $\text{Au (100)}/50 \text{ mol m}^{-3} \text{ H}_2\text{SO}_4 + 1 \text{ mol m}^{-3} \text{ CdSO}_4$.

Fig. 7 Anodic voltammograms obtained after different holding times at -1100 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ at 333 K. Systems: $\text{Au (100)}/50 \text{ mol m}^{-3} \text{ H}_2\text{SO}_4 + 1 \text{ mol m}^{-3} \text{ CdSO}_4$. Sweep rate: 50 mV s^{-1} .

Fig. 8 X-ray diffraction patterns of the Au (100) sample maintained at -1100 mV in $50 \text{ mol m}^{-3} \text{ H}_2\text{SO}_4 + 1 \text{ mol m}^{-3} \text{ CdSO}_4$ solution at -1100 mV vs. $\text{Hg}/\text{Hg}_2\text{SO}_4$ for 1 h at 333 K by low-angle XRD (0.5°).

4. Conclusions

We investigated the inward diffusion of UPD Cd adatoms into a Au (100) electrode in contact with 50 mol m^{-3} sulfuric acid solution at -1100 mV by anodic voltammetry at temperature range from 295 to 333 K, and also by EQCM analysis and XRD. From the results of these studies, the following conclusions were drawn.

The amount of the UPD Cd into a Au (100) electrode obtained from the anodic voltammetry agrees fairly well with that calculated from the EQCM analysis. This means that the amount of UPD Cd adatoms can be estimated from the total anodic charge obtained from the voltammograms.

From the anodic voltammetry, we found that inward diffusion consists of two steps. One is a very fast step, which is the diffusion of UPD Cd into a Au (100) electrode at the thin surface layer; the activation energy is $\cong 70 \text{ kJ mol}^{-1}$. The other is much slower step, which is governed by the bulk diffusion step with the activation energy $\cong 110 \text{ kJ mol}^{-1}$, which agrees well with that for the bulk diffusion of Cd atoms in a Au–Cd compound.

The structure of the Au (100) surface formed by maintaining at -1100 mV for 1 h at 333 K was also confirmed to be β Au–Cd by low-angle XRD.

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