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# Epitaxial Growth of Palladium Layer on an Au(100) Electrode

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## Abstract

The electrochemical deposition process of palladium from a  $\text{PdCl}_4^{2-}$  complex on an Au(100) substrate was investigated using in situ scanning tunneling microscopy (STM). The reactant, i.e., the  $\text{PdCl}_4^{2-}$  complex, was found to adsorb on the Au(100) surface with an ordered structure in the potential region where neither a cathodic nor anodic current flowed. The electrochemical deposition of palladium on the Au(100) proceeded at potentials more negative than 1.0 V. The electrodeposition of the first palladium layer started not only on the terrace but also on gold islands which were formed as a result of the lifting process of the reconstructed Au(100) surface and then proceeded two-dimensionally. The following palladium layer was found to mainly grow from the deposited palladium region on top of the gold islands. The shape of the gold island can be identified even after four palladium layers were deposited. The bulk and surface structures of the deposited palladium layer were characterized by X-ray diffraction (XRD) and the copper underpotential deposition (UPD) reaction, respectively, and the formation of the Pd(100) phase with a (1×1) surface structure was confirmed.

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## 1. Introduction

Metal deposition on metal and semiconductor substrates is important not only for fundamental science but also for various industrial applications such as electronics, catalysis, sensors and surface finishing. Although metal deposition by physical means such as vacuum deposition is commonly used [1], metal deposition by an electrochemical method should be more economical and convenient than the growth in ultrahigh vacuum (UHV) because the expensive UHV environment is not necessary. Unfortunately, however, it is generally believed that the quality of electrodeposited metal layer is poorer than that of physically deposited one [2]. The morphology of the electrodeposited metal layer is controlled by many factors such as deposition potential, current density, concentration of metal ion/complex and nature of the additives and substrate. To establish methods to grow high quality metal deposits with a controlled structure, it is essential to understand the electrochemical deposition process with atomic/molecular resolution. For this purpose, many in situ surface techniques such as STM [3, 4], atomic force microscopy (AFM) [3-7] and surface X-ray scattering (SXS) [8-11] are widely applied during the investigation of an electrochemical deposition process on an atomic/molecular scale. Recently, we reported that the electrochemical deposition of palladium [12-14] and platinum [15, 16] layers on an Au(111) electrode surface epitaxially proceeded if their chlorinated complexes, i.e., tetrachloropalladate ( $\text{PdCl}_4^{2-}$ ) and hexachloroplatinate ( $\text{PtCl}_6^{2-}$ ), respectively, were used as reactants. We proposed that the strongly adsorbed  $\text{PdCl}_4^{2-}$  species, which was found both on the Au(111) substrate and on the deposited palladium layer surfaces with the  $(\sqrt{7}\times\sqrt{7})R19.1^\circ$

structure, play an important role in the layer-by-layer growth during palladium deposition [17]. Baldauf and Kolb found that the electrochemical growth of palladium on an Au(100) surface also epitaxially proceeded but no STM image of palladium deposition on Au(100) was given in their paper [17]. Thus, the detailed epitaxial growth mechanism of palladium on an Au(100) substrate has not yet been clarified.

Here, we investigated the adsorption and electrochemical reduction of  $\text{PdCl}_4^{2-}$  on an Au(100) electrode using in situ STM. We found that an ordered adlayer of the  $\text{PdCl}_4^{2-}$  complex, i.e., the reactant of the electrodeposition, is formed on an Au(100) surface as on an Au(111) surface but with a structure different from that on Au(111) and the electrochemical deposition of palladium from  $\text{PdCl}_4^{2-}$  on an Au(100) substrate in  $\text{H}_2\text{SO}_4$  solution proceeds in a layer-by-layer mode.

## 2. Experimental

An Au(100) single crystal was prepared using Clavilier's method [18]. It was mechanically polished and annealed in an electric furnace for at least 4 hours at ca. 800 °C under an air stream. Before each measurement, the electrode was annealed by a gas-oxygen flame for a few seconds and then quenched in argon saturated Milli-Q water.

Electrolyte solutions were prepared by using H<sub>2</sub>SO<sub>4</sub> (Suprapure reagent grade, Wako Pure Chemicals), K<sub>2</sub>PdCl<sub>4</sub> (Reagent grade, Wako Pure Chemicals), CuSO<sub>4</sub> (Reagent grade, Wako Pure Chemicals) and Milli-Q water.

The in situ electrochemical STM measurements were carried out using a NanoScope E (Digital Instruments) control unit, a PicoSPM (Molecular Imaging) scanning unit with an air tight chamber and solution inlet tubes and a home-made electrochemical STM cell which can accommodate a single crystal electrode. A small quasi-reversible hydrogen electrode and a platinum wire were used as the reference and the counter electrode, respectively. The electrolyte solution was deaerated by passing purified argon gas for at least 20 min before it was introduced into the STM cell. The electrochemical potentials of the Au(100) substrate and STM tip were independently controlled by a bipotentiostat (PicoSTAT, Molecular Imaging). The STM tips were mechanically cut Pt/Ir wire (80/20,  $\phi = 0.25$  mm) insulated with nail polish. Before each measurement, purified argon gas was pumped into to the STM chamber to purge the oxygen.

The STM images with atomic resolution were recorded as current images in a constant height mode and wide range STM images were recorded as height images in a constant current

mode. The STM images with atomic resolution were only lowpass filtered. No additional filter treatment was carried out.

For the electrochemical measurements, a three-electrode cell was used. The single crystal electrode surface was contacted to the solution through a meniscus, i.e., a dipping method. The electrochemical potential was controlled by a potentiostat (Hokuto Denko, HA-151) and external potential modulation was provided by a function generator (Hokuto Denko, HB-111). A quasi-reversible hydrogen electrode and a platinum wire were used as the reference and counter electrode, respectively. All the potentials in this paper are presented with respect to the reversible hydrogen electrode (RHE).

The XRD measurement was carried out using a RINT-2200 (RIKAKU) with a four-circle diffractometer. More detailed experimental conditions can be found in our previous papers [12, 16].

### 3. Results and Discussion

#### 3.1 Adsorption of $\text{PdCl}_4^{2-}$ Species on an Au(100) Electrode.

Figure 1 shows a cyclic voltammogram (CV) of an Au(100) electrode in 50 mM  $\text{H}_2\text{SO}_4$  solution. The Au(100) electrode surface was in contact with the solution while the electrode potential was kept at 0.1 V and then the potential was scanned in the positive direction to +1.7 V at  $50 \text{ mVs}^{-1}$ . A small anodic peak shown by an arrow in Fig. 1 was observed at 0.63 V which is known to be associated with the lifting process of the reconstructed hexagonal (hex) Au(100) surface to the (1×1) surface [19-21]. The anodic current peaks observed at 1.38 and 1.42 V in the positive potential scan and a cathodic peak observed at 1.18 V in the negative potential scan are attributed to the formation and the reduction of gold oxide on the Au(100) surface, respectively. The profile of the CV is in good agreement with the results previously reported for an Au(100) electrode [22].

Figure 2 shows (a) wide scan ( $300 \times 300 \text{ nm}^2$ ) and (b) high resolution ( $5 \times 5 \text{ nm}^2$ ) STM images of the Au(100) surface at 0.95 V in 50 mM  $\text{H}_2\text{SO}_4$  solution. Many gold islands with monoatomic height were observed on the Au(100) surface as shown in Fig. 2(a). These gold islands were formed as a result of the reconstruction lifting of the Au(100) surface from hex to (1×1) because the surface atomic density of the (1×1) structure is lower than that of hex by 25 % [19-21]. The atomically ordered Au(100)-(1×1) structure (nearest-neighbor distance of ca. 0.29 nm) shown in Fig. 2(b) was observed both on the terrace and on the gold islands at 0.95 V in the same solution.

Figure 3 shows (a)  $20 \times 20 \text{ nm}^2$  and (b)  $5 \times 5 \text{ nm}^2$  wide STM images of the Au(100) electrode obtained after a 50 mM  $\text{H}_2\text{SO}_4$  solution containing 1.0 mM  $\text{PdCl}_4^{2-}$  was added to the STM cell (final concentration of  $\text{PdCl}_4^{2-}$  of ca. 0.5 mM) at +1.05 V. An ordered structure different from that of the Au(100) substrate was observed on the same electrode. This structure was observed only in the solution containing the  $\text{PdCl}_4^{2-}$  complex. A wide scan STM investigation showed that the surface morphology on both the Au(100) terraces and gold islands was not affected by the addition of the  $\text{PdCl}_4^{2-}$  containing solution, showing that the Au(100)-(1 $\times$ 1) surface was stable and palladium deposition did not proceed at +1.05 V in this solution. Thus, the structure observed in Fig. 3 should be attributed to the adsorbed  $\text{PdCl}_4^{2-}$  on the Au(100)-(1 $\times$ 1) surface. The (001) and (010) directions of the Au(100) substrate determined by the direction of the step lines are shown by arrows in the high resolution image (Fig. 3(b)). The unit lattice of the adlayer was estimated from a Fourier transformed 2D spectrum for Fig. 3(b) and the estimated unit lattice was superimposed on the image as a white box. The spacing of the unit lattice along with the long and short sides were ca. 1.47 nm and ca. 1.03 nm, respectively. Figure 3(c) shows a ball model of the  $\text{PdCl}_4^{2-}$  complex adsorbed on the Au(100)-(1 $\times$ 1) surface. The adlayer structure observed here was different from that observed on the Au(111)-(1 $\times$ 1) surface, i.e., the Au(111)-( $\sqrt{7} \times \sqrt{7}$ )R19.1 $^\circ$  structure [12, 15]. The coverage of the  $\text{PdCl}_4^{2-}$  complex adsorbed on the Au(100)-(1 $\times$ 1) surface was slightly lower than that on Au(111). It should be mentioned that the STM image of the ordered adlayer structure on the Au(100) surface was hard to obtain when the concentration of  $\text{PdCl}_4^{2-}$  species was lower than 0.05 mM, while the ordered

the  $\text{PdCl}_4^{2-}$  adlayer was observed on the Au(111) surface under the same conditions. These results suggest that the adsorption energy and the interaction between the adsorbed  $\text{PdCl}_4^{2-}$  complex on the Au(100) surface is weaker than that on the Au(111) surface.

### 3.2 *Electrochemical Deposition of Palladium.*

#### 3.2.1 *Electrochemical Behavior*

Figure 4 shows a cyclic voltammogram of an Au(100) electrode in 50 mM  $\text{H}_2\text{SO}_4$  solution containing 0.1 mM  $\text{PdCl}_4^{2-}$ . The electrode was in contact with the solution at +1.0 V, where neither a cathodic nor anodic current flowed, and then the potential was swept in the negative direction by  $5 \text{ mV s}^{-1}$ . A cathodic current started to flow as the potential was made more negative than +1.0 V. After two cathodic peaks were observed at 0.90 and 0.83 V, a limiting current flowed up to ca. +0.35 V. The cathodic current flowed in this potential region should be due to the reduction of  $\text{PdCl}_4^{2-}$  to palladium on the Au(100) surface [12]. A cathodic peak with a shoulder was observed at +0.23 V. An anodic peak was observed at +0.24 V when the potential was swept in the positive direction from +0.1 V. The redox peaks in this potential region are due to hydrogen adsorption/desorption as reported by Baldauf and Kolb [17]. The amount of deposited palladium estimated from the charge during the potential sweep from +1.0 to +0.1 V was ca. 1.5 monolayers [23]. The charge for hydrogen adsorption and desorption was estimated to be 191 and 205  $\mu\text{C cm}^{-2}$ , respectively [23]. These values are in agreement with those expected for hydrogen adsorption and desorption on an ideal Pd(100)-(1 $\times$ 1) surface. It was found that the

reaction of the hydrogen adsorption and desorption is actually sensitive to the surface structure and thickness of palladium thin layer deposited. In the more positive potential region, a relatively constant cathodic current flowed up to +0.82 V. An anodic current started to flow at this potential and an anodic current peak was observed at +1.03 V. Our previous EQCM results on the Au(111) surface [12] suggest that the relatively constant cathodic current in this potential region was also due to the deposition of palladium and the anodic current was due to the dissolution of a deposited palladium layer.

### 3.2.2. *In situ STM Investigation*

Figure 5 shows STM images ( $300 \times 300 \text{ nm}^2$ ) of an Au(100) surface obtained in 50 mM  $\text{H}_2\text{SO}_4$  solution containing 0.5 mM  $\text{PdCl}_4^{2-}$ . The electrochemical potential of the STM tip was held at +1.05 V during the measurements to avoid the deposition of palladium on the STM tip. It took ca. 45 s to capture one image. The scan direction and the cross section along the white broken line are shown at the upper-right side and bottom side of each image, respectively. Figure 5(a) is an STM image obtained at +1.0 V when no palladium deposition took place. There are a number of gold islands on the surface as observed in Fig. 2(a). The cross section in Fig. 5(a) shows that the height of the gold islands is the same as that of a gold monoatomic step (0.20 nm) as expected.

Figures 5(b) - 5(g) show STM images sequentially obtained during the palladium deposition process. As soon as the potential of the Au(100) substrate was stepped from +1.0 to

+0.80 V as indicated by a thick arrow in Fig. 5(b), palladium nuclei were generated both on the wide terrace and on the gold islands (see cross section I). The height of the palladium nuclei corresponded to that of a palladium monoatomic step (0.19 nm). The first layer of palladium two-dimensionally grew from these nuclei. As shown in the cross section II in Fig. 5(b), the growth of the first palladium layer on the Au(100) surface was completed within 10 s after the potential step.

Figure 5(c) shows an STM image recorded immediately after the Fig. 5(b). The time after the potential pulse corresponding to the top and bottom of the STM image is indicated on the right hand side of each image. The second palladium layer started to grow at the moment corresponding to the the upper portion of the image. As shown in the cross section in Fig. 5(c), the second layer of palladium seemed to grow laterally from the deposited palladium layer just on top of the gold islands. Growth of the second layer of palladium on the gold terrace was completed within ca. 30 s. It was noted that while the gold terraces were covered with two layers of palladium, the gold islands were only covered with one monolayer of palladium. At this stage, the height difference between the two regions is very small but still distinguishable, reflecting the difference in atomic diameters of gold (0.288 nm) and palladium (0.275 nm). The difference in the local electronic states on the electrode surface may also contribute to the observed STM images but the details are not clear.

Figure 5(d) shows an STM image between 103 and 148 s after the potential step. A cross section of Fig. 5(d) clearly shows that the third layer of palladium was also initiated from the

deposited palladium layer on top of the gold islands and grew laterally. As shown in the subsequent STM images in Figs. 5(e) (291~395 s) and 5(f) (635~680 s), each palladium island grew laterally and eventually merged together. Completion of the third palladium layer took more than 1000 s which is much longer than the time required for the growth of the first and second layers of palladium. The decrease in the growth rate of palladium should be attributed to the decrease in the local concentration in the region where the STM tip was scanned as discussed in our previous paper [14]. The two-dimensional growth process of the fourth palladium layer was clearly observed on the right hand portion of the STM images shown in Figs. 5(f) and 5(g) (1110~1155 sec). Even after four layers of palladium were deposited on the Au(100) terrace and three layers of palladium on the gold islands, the shape of the gold islands was still distinguishable.

Thus, a palladium layer grew on the Au(100)-(1 $\times$ 1) surface in a layer-by-layer mode as was the case on the Au(111) electrode. Although we are unable to observe an ordered adlayer of an adsorbed PdCl<sub>4</sub><sup>2-</sup> complex on the deposited palladium layer by STM so far, we expect the existence of the adlayer which plays a similar role for the two-dimensional growth during electrochemical deposition of palladium on the Au(100) surface as was observed on the Au(111) surface [12].

### *3.3 Characterization of Deposited Palladium Layer.*

The bulk structure of the deposited palladium layer was examined using XRD. Figure 6

shows the XRD patterns of (a) an Au(100) single crystal, (b) an Au(100) single crystal on which ca. 73 monolayers of palladium was electrochemically deposited at 0.7 V for 1 hour in a 50 mM H<sub>2</sub>SO<sub>4</sub> solution containing 1 mM PdCl<sub>4</sub><sup>2-</sup> (Pd(73ML) / Au(100)), and (c) a bare polycrystalline Pd foil. The assignments based on the JCPDS data are given for the respective diffraction peaks in the figure [24, 25]. Only the Au(200) and Au(400) peaks were observed for the Au(100) single crystal. In addition to the Au(200) and Au(400) peaks, the Pd(200) peak was observed in the XRD pattern of the Pd(73 ML)/Au(100). No other peak due to palladium such as Pd(111), Pd(220), and Pd(311), which are stronger than the Pd(200) peak in the case of the polycrystalline palladium, was obtained. Thus, it is confirmed that the Pd(100) phase was electrochemically deposited on the Au(100) substrate.

The surface structure of the palladium deposited layer was also examined by recording a CV for the underpotential deposition (UPD) of copper. The position and shape of the UPD peak is known to be very sensitive to the surface structure and order [26, 27]. After the deposition of palladium in 50 mM H<sub>2</sub>SO<sub>4</sub> solution containing 0.1 mM PdCl<sub>4</sub><sup>2-</sup> at 0.7 V for 30 min (ca. 5 ML), the electrode was rinsed with Milli-Q water. The CV of copper UPD was recorded in another cell that contained a 50 mM H<sub>2</sub>SO<sub>4</sub> + 5 mM Cu<sup>2+</sup> solution. Sharp cathodic and anodic peaks with a full width at half maximum (FWHM) of ca. 17 and 13 mV were observed at 0.58 and 0.60 V, respectively (Fig. 7). The CV of copper UPD on a polycrystalline palladium is totally different from this CV. Furthermore, the position of the copper UPD peaks are completely different from those of copper UPD on the electrodeposited palladium layer on Au(111). The copper UPD

process on a Pd(100) single crystal electrode was studied in 0.5 M NaClO<sub>4</sub> + 10<sup>-2</sup> M HClO<sub>4</sub> + 10<sup>-3</sup> M Cu<sup>2+</sup> solution and two pairs of sharp peaks were observed at 0.49/0.50 and 0.27/0.29 V [26, 27]. The former peaks seem to correspond to the peaks observed in the present study. The small differences in peak potentials of the former peaks reflect the difference in the electrolyte solution. The copper stripping charge was 192 μC cm<sup>-2</sup> which is in good agreement with the expected value (210 μC cm<sup>-2</sup>) for the Pd(100)-(1×1) surface structure [27]. Thus, it was confirmed that the deposited palladium layer on the Au(100) electrode was the epitaxially grown Pd(100) phase with a (1×1) surface structure. It should be noted here that ca. 4.5% lattice mismatch is expected between the lattice constants of Au(100) (0.288 nm) and Pd(100) (0.275 nm). Since the difference is too small to be investigated by STM, we are now investigating this point by surface X-ray scattering (SXS) using SOR. Preliminary result for Pd layer on Au(111) showed that the unit lattice of the 1st Pd layer is of underlying Au(111) while that of the 8th layer is of bulk Pd(111) [28]. The detailed SXS investigation on palladium layers on Au(100) is now in progress.

#### **4. Conclusions**

Electrochemical deposition of palladium from PdCl<sub>4</sub><sup>2-</sup> was investigated using in situ STM measurements. The PdCl<sub>4</sub><sup>2-</sup> complex was found to adsorb on the Au(100) surface with an ordered adlayer structure. The electrodeposition of the first palladium layer on the Au(100) substrate was initiated from both the wide terrace sites and gold islands, which were originally formed as a

result of the lifting process of the reconstructed Au(100) surface, and then proceeded two dimensionally. The following palladium layer was found to mainly grow from the sites on top of the gold islands. These islands work as nucleation centers for the lateral growth of palladium. The shape of the gold island was distinguishable even after four monolayers of palladium were deposited. Characterizations by XRD and copper UPD proved the formation of the Pd(100) phase with a (1×1) surface structure on the Au(100)-(1×1) substrate.

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*submitted.*

## Figure Captions

Figure 1. Cyclic voltammogram of an Au(100) electrode in 50 mM H<sub>2</sub>SO<sub>4</sub> solution. Potential sweep rate: 50 mV s<sup>-1</sup>.

Figure 2. STM images of the Au(100)-(1×1) surface (a) with wide range (300 × 300 nm<sup>2</sup>, a height image in a constant current mode) and (b) with atomic resolution (5 × 5 nm<sup>2</sup>, a current image in a constant height mode) at 0.95 V in 50 mM H<sub>2</sub>SO<sub>4</sub> solution. Fig. (b) was lowpass filtered. No additional filter treatment was carried out.

Figure 3. STM images of (a) 20 × 20 nm<sup>2</sup> and (b) 5 × 5 nm<sup>2</sup> wide (current images in a constant height mode) of the Au(100) surface at 1.05 V in a 50 mM H<sub>2</sub>SO<sub>4</sub> solution containing ca. 0.5 mM PdCl<sub>4</sub><sup>2-</sup>. The inset of (b) is the Fourier transformed 2D spectrum. A unit lattice determined from the spectrum is superimposed on the image with a white box (b). Images were lowpass filtered. No additional filter treatment was carried out. (c) A ball model of the PdCl<sub>4</sub><sup>2-</sup> complex adsorbed on the Au(100)-(1×1) surface.

Figure 4. Cyclic voltammogram of the Au(100) electrode in 50 mM H<sub>2</sub>SO<sub>4</sub> solution containing 0.1 mM PdCl<sub>4</sub><sup>2-</sup>. Potential sweep rate: 5 mV s<sup>-1</sup>.

Figure 5. (a) An STM image ( $300 \times 300 \text{ nm}^2$ , a height image in a constant current mode) of the Au(100) substrate at +1.0 V in a 50 mM  $\text{H}_2\text{SO}_4$  solution containing ca. 0.5 mM  $\text{PdCl}_4^{2-}$ . (b)~(g) STM images ( $300 \times 300 \text{ nm}^2$ , height images in a constant current mode) obtained sequentially during the palladium deposition process on the Au(100) substrate in the same solution. Time after the potential pulse corresponding to the top and bottom of the STM image is indicated on the right hand side of each image. The electrochemical potential of the STM tip was held at 1.05 V during the measurements. The cross section along the broken white line in each figure is shown below each image.

Figure 6. XRD patterns of (a) an Au(100) single crystal, (b) an Au(100) single crystal after 73 ML of palladium was electrodeposited at 0.7 V for 1 hour in 50 mM  $\text{H}_2\text{SO}_4$  solution containing 1 mM  $\text{PdCl}_4^{2-}$  and (c) a polycrystalline Pd foil.

Figure 7. Cyclic voltammogram of the deposited palladium layer (ca. 5 ML) on an Au(111) electrode in a 5 mM  $\text{CuSO}_4 + 50 \text{ mM } \text{H}_2\text{SO}_4$  solution. Potential sweep rate:  $5 \text{ mVs}^{-1}$ .





























