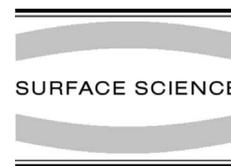




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Spontaneous deposition of Pd on a Ru(0001) surface

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Abstract

Spontaneous deposition of Pd on a Ru(0001) single crystal surface has been demonstrated by an in situ scanning tunneling microscopy technique. The immersion of an ultrahigh vacuum prepared Ru single crystal in a palladium ion containing solution results in a formation of an epitaxial and textured multilayer Pd deposit without applying an external potential. The amount of deposited Pd can be indirectly controlled by the amount of Pd ions confined in the solution volume in contact with a Ru surface. The results suggest that the initial Pd growth involves formation of an ordered monolayer, while further growth results in formation of a three-dimensional Pd deposit. © 2001 Published by Elsevier Science B.V.

Keywords: Scanning tunneling microscopy; Surface chemical reaction; Growth; Palladium; Ruthenium; Metallic films

1. Introduction

Immersion of clean noble metal surfaces in metal cation-containing solutions can produce “spontaneously” adlayers of various metals strongly interacting with the substrate without the application of external potential. “Spontaneous” deposition of metal adlayers on noble metal surface has been recognized as a potential method for modifying surface catalytic properties and preparing bimetallic electrode surfaces [1–6]. In some cases, noble metal adlayers can be deposited spontaneously on noble metal substrates, as exemplified by Pd deposition on Pt [1,3,4] and Ru deposition on Pt single crystals [5,6]. In the latter

case, the electrocatalysts with a considerable activity for methanol oxidation have been obtained with Ru coverage that could not exceed 20% [2,5]. For spontaneous deposition of Pd on a Pt(111) electrode, monolayer [3], or submonolayer [4,7] coverages were reported. Spontaneous deposition was recently also demonstrated for the Pt/Ru(0001) system [8,9]. Surprisingly, submonolayer-to-multilayer Pt deposits were found in this case. As an alternative to the spontaneous deposition method, a spontaneous replacement of an underpotentially deposited metal adlayer by a more noble metal monolayer has been proposed as another convenient way of controlled modification of a catalyst surface [10]. The possibility of obtaining active electrocatalysts with considerably reduced noble metal loading is a particularly interesting aspect of these deposition techniques.

In this letter we demonstrate spontaneous deposition of Pd on a Ru(0001) single crystal

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surface, determined by in situ scanning tunneling microscopy (STM). Palladium and ruthenium are important catalytic materials and Pd–Ru bimetallic surfaces obtained by a spontaneous deposition method could serve as an alternative to conventional Pt–Ru electrocatalysts [11]. As demonstrated below, multilayer Pd deposits on Ru(0001) can be obtained, which has not been observed for the Pd/Pt(111) [3,4] and Ru/Pt(111) [2,5] spontaneous deposition systems. The spontaneously deposited Pd films are epitaxial with the Ru substrate. The initial deposition stage proceeds through a formation of a several wetting monolayers, which is also observed in electrodeposition of Pd on Au(111) [12,13], and in vacuum deposition of Pd on Ru(0001) [14] and Pt(111) [15].

2. Experimental

The working electrode was a Ru(0001) single crystal $8 \times 3 \text{ mm}^2$ disk polished with diamond pastes down to $0.3 \mu\text{m}$, obtained from Metal Crystals and Oxides, Cambridge, England. The single crystal was additionally oriented to better than 0.1° . The single crystal electrode surface was prepared in ultrahigh vacuum (UHV), following the standard procedure for Ru [16]. It consisted of two cycles of argon ion sputtering at room temperature and annealing at 1400°C , followed by five cycles of oxygen adsorption and desorption in an oxygen atmosphere of 10^{-7} Torr at 500°C and 1400°C , respectively. A final flash annealing was done in UHV at 1400°C to remove the residual oxygen from the surface. The crystal was allowed to cool down in the vacuum chamber. After that, the chamber was filled with ultrapure Ar and the crystal was transferred from the UHV chamber into an Ar-filled glove box where it was immersed in solution containing $[\text{PdCl}_4]^{2-}$ ions. After the emersion from the $[\text{PdCl}_4]^{2-}$ solution, the crystal was thoroughly rinsed with $0.1 \text{ M H}_2\text{SO}_4$ solution and ultrapure water, protected by a water drop, and transferred to the STM cell. Solutions were prepared from Optima* sulfuric acid from Fisher and MilliQ UV-plus water (Millipore). An $\text{Ag}|\text{AgCl}|\text{KCl}(3 \text{ M})$ electrode was used as a reference electrode in all experiments and all potentials

are quoted with respect to its potential. The in situ STM studies were performed using a Molecular Imaging Pico STM with a 300S scanner and Molecular Imaging Model 300S Pico Bipotentiostat. The Teflon cell had an exposed area of $\approx 0.3 \text{ cm}^2$ and a volume of $\approx 1.5 \text{ cm}^3$. Prior to each experiment, an STM tip was prepared by etching a 80:20 Pt:Ir wire in a CaCl_2 solution and insulated with Apiezon wax. A Pt wire was used as a pseudo reference electrode. Its potential was determined against an Ag/AgCl , Cl^- reference electrode in a given solution.

3. Results and discussion

A representative image of the Ru(0001) surface in $0.1 \text{ M H}_2\text{SO}_4$ solution is shown in Fig. 1. The image was recorded at potential of -0.150 V , which is in the double layer region of a Ru(0001) surface [17,18]. The monoatomic steps running in the $\langle 11\bar{2}0 \rangle$ direction are clearly seen. Most of the steps are equally spaced and separated with the atomically flat terraces yielding an impression of a well sputter-annealed Ru(0001) surface.

The spontaneous deposition of Pd on Ru(0001) was carried out from $x \text{ M}$ ($x = 10^{-3}$, 10^{-4} , 3×10^{-5}) $[\text{PdCl}_4]^{2-} + 0.1 \text{ M H}_2\text{SO}_4$ solution. The Ru surface was brought into contact with 0.1 ml (two droplets) of a palladium containing solution,

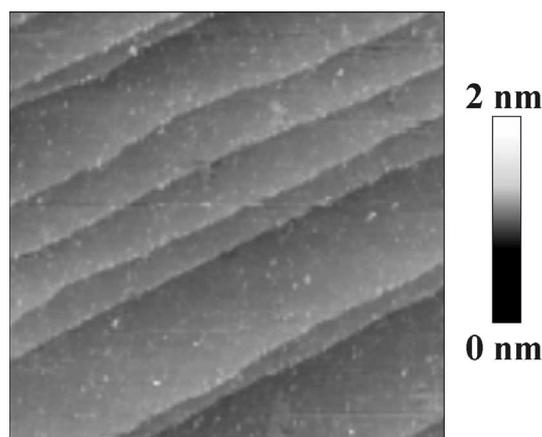


Fig. 1. STM image of a Ru(0001) surface in $0.1 \text{ M H}_2\text{SO}_4$ solution. Image size: $260 \times 260 \text{ nm}^2$.

immediately after the transfer from the UHV chamber into an Ar filled glove box. The Pd ion solution covered the entire surface of the Ru crystal, and its exact volume provided an indirect way to control the amount of Pd that could be spontaneously deposited. In the limiting case, all Pd ions would be deposited. The maximum amount of deposited Pd was calculated in monolayer (ML) units by using the surface area of the Ru crystal of 0.5 cm^2 . The time that the crystal was kept in contact with the Pd containing solution was usually 3 min. Subsequently, the crystal was rinsed with $0.1 \text{ M H}_2\text{SO}_4$ and ultrapure water and transferred to the STM cell. Immersion times longer than 3 min did not produce any difference in morphology and the amount of the deposited Pd for a given solution concentration, indicating complete deposition of Pd. No additional procedure was used to enhance convection in the solution.

Representative morphology of a spontaneously formed Pd deposit in a $10^{-3} \text{ M [PdCl}_4\text{]}^{2-} + 0.1 \text{ M H}_2\text{SO}_4$ solution is shown in Fig. 2A. It is seen that the Pd deposit completely covers the Ru surface. The deposit consists mainly of a large number of Pd facets that are merged in a continuous but textured layer. A common angle among the facets' edges of 120° is visible over the entire surface. This is usually an indication that the facets have a (111) orientation, which may indicate that Pd spontaneously forms an epitaxial deposit on Ru(0001) surface. A closer inspection of the fac-

eted deposit shows a terrace-step morphology with a number of holes in the terraces (Fig. 2B). Focusing the STM tip on one of the terraces yields images of an atomically ordered surface. The insert in Fig. 2B shows the atomic resolution obtained on the terrace marked by A in Fig. 2B. The atomic arrangement has a close packed hexagonal structure, which confirms the {111} orientation of the Pd facets, i.e., the epitaxy of a Pd deposit grown on a Ru substrate. The STM data clearly show that Pd can form spontaneously a multilayer deposit on a Ru surface, but the Pd coverage in these films is difficult to determine accurately.

In order to control the amount of deposited Pd, a freshly prepared Ru surface was covered with a 0.1 ml of a $10^{-4} \text{ M [PdCl}_4\text{]}^{2-} + 0.1 \text{ M H}_2\text{SO}_4$ solution containing the Pd amount equivalent to approximately 8–10 ML. A representative image of the Pd deposit is shown in Fig. 3A and B. It is obvious that less Pd was spontaneously deposited than on the sample in Fig. 2 because less Pd was available in the solution. The Pd deposit is mostly in the shape of 3–7 ML high clusters, which are partially interconnected. From these STM images it is not possible to determine whether the Pd clusters are formed directly on the Ru surface or on a Pd adlayer formed prior to their nucleation. A closer look at the morphology of the deposit in Fig. 3B, however, suggests that in the very initial stage of growth Pd can form one or several wetting layers on Ru surface. A similar observation has

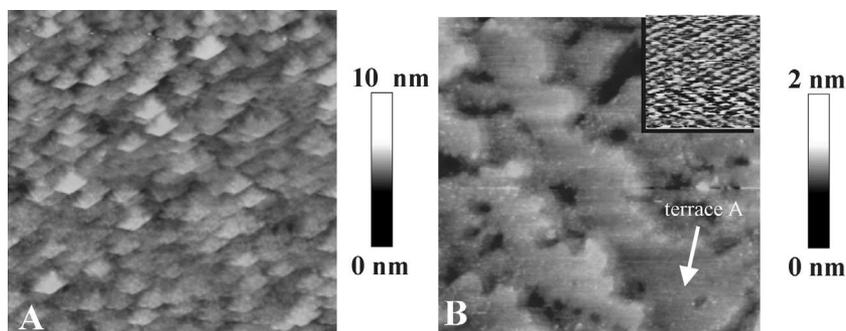


Fig. 2. STM images: (A) $500 \times 500 \text{ nm}^2$ and (B) $60 \times 60 \text{ nm}^2$ of a Pd layer spontaneously deposited on Ru(0001) from $1 \text{ mM H}_2\text{PdCl}_4 + 0.1 \text{ M H}_2\text{SO}_4$ (see text for details). Insert ($3.4 \times 3.4 \text{ nm}^2$) in image (B) shows atomic structure on a terrace A. All images are recorded at open circuit potential in $0.1 \text{ M H}_2\text{SO}_4$ solution.

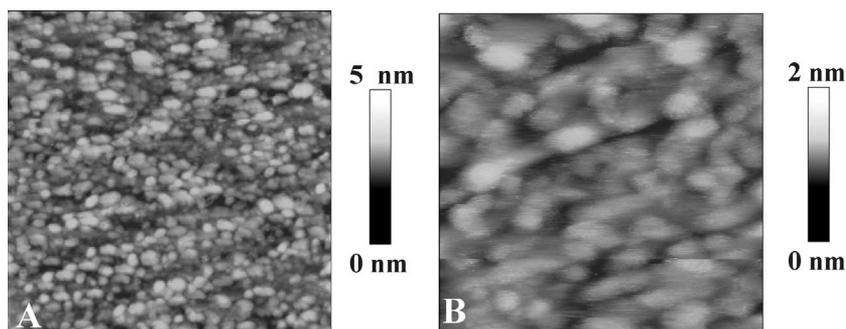


Fig. 3. STM images (A) $100 \times 100 \text{ nm}^2$ and (B) $25 \times 25 \text{ nm}^2$ of a Pd adlayer spontaneously deposited on Ru(0001) from 0.1 mM H_2PdCl_4 + 0.1 M H_2SO_4 (see text for details). Images are recorded at open circuit potential in 0.1 M H_2SO_4 solution.

been reported for the case of initial Pd growth on Au(111) [12,13].

In order to clarify this question, an experiment was performed where the total amount of Pd in a $3 \times 10^{-5} \text{ M}$ $[\text{PdCl}_4]^{2-}$ solution covering the Ru crystal was equivalent to approximately 3 ML. A representative STM image of the Pd deposit is shown in Fig. 4A. A much more uniform morphology of the deposit is obtained than for solutions of higher concentrations. The entire surface appears to be covered by a 1–2 ML high Pd film decorated with small two-dimensional (2D) Pd clusters of monoatomic height. At a few isolated sites the cluster height is greater than 1 ML. Since the maximum amount of Pd that could be deposited is less than 3 ML, it is not surprising that the step-terrace morphology of the underlying Ru substrate is easily recognized (marked with an ar-

row in Fig. 4A). The STM image with atomic resolution shown in Fig. 4B was taken on a flat part of terrace indicated in Fig. 4. The terrace has a close packed hexagonal atomic arrangement. A clear distinction whether the imaged terrace is a Ru(0001) or Pd(111) surface (Fig. 4A) is not possible from the STM data due to the similar atomic dimensions of Pd and Ru (the difference is only 1.8% [19]). Our previous in situ STM studies of a Ru(0001) surface in acidified solutions [8,9] did not resolve any ordered structure of a Ru surface due to a strong interaction of Ru with H_2O molecules, which apparently causes a formation of a disordered RuOH adlayer. Indirectly, this means that in this experiment no ordered structure of Ru(0001) is expected to be resolved under the same conditions. However, the STM data show the opposite, leading to the conclusion that the top

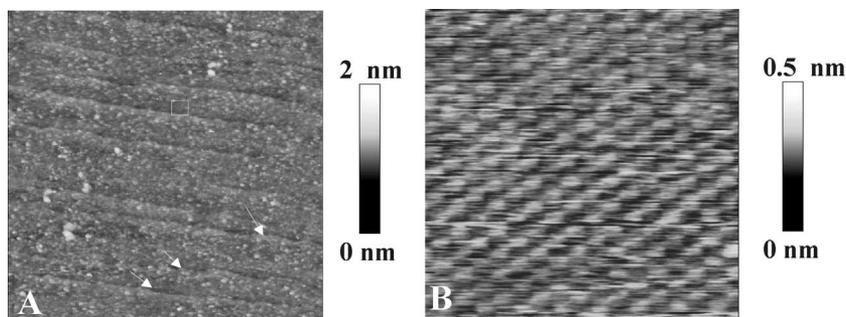
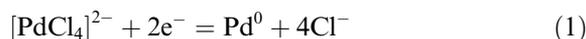


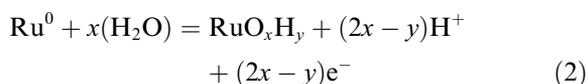
Fig. 4. STM images (A) $170 \times 170 \text{ nm}^2$ of a Pd adlayer spontaneously deposited on Ru(0001) from 0.03 mM H_2PdCl_4 + 0.1 M H_2SO_4 (see text for details). Atomically resolved image (B) $3.4 \times 3.4 \text{ nm}^2$ obtained at the square in the image (A). Arrows at the image (A) indicate underlying Ru morphology. Images are recorded at open circuit potential in 0.1 M H_2SO_4 solution.

layer on the terrace in Fig. 4 is Pd(1 1 1), and that the initial growth of Pd involves the formation of one or two wetting monolayers. This is in agreement with the results from a UHV study of ultrathin Pd films on a Ru(000 1) surface showing that the initial growth Pd proceeds by formation of several epitaxial Pd monolayers, pseudomorphic with the Ru substrate [14]. In addition, a hydrogen adsorption/desorption process, seen in cyclic voltammetry measurements with this surface (not shown), can only be due to Pd since Ru(000 1) does not show such a process in the same potential region.

It is interesting that spontaneous deposition of Pd on Ru(000 1) surface does not occur on a Ru(000 1) crystal with a RuOH surface layer. Even immersion in 0.1 M H₂SO₄, 0.1 M HClO₄ or pure H₂O for short time (1–30 min) prior to contact with [PdCl₄]²⁻ ions has the same effect. This suggests that only a freshly prepared metallic Ru(000 1) surface in contact with the [PdCl₄]²⁻-containing solution is capable of depositing Pd spontaneously. It was recently shown that Ru(000 1) strongly adsorbs H₂O and forms between 0.0 and 0.3 V an adlayer that has an oxygen plane slightly farther from the Ru(000 1) surface than the oxygen plane in RuOH that exists above 0.3 V [8,9]. Such an adlayer can preclude spontaneous deposition of Pd. The interaction of Ru with H₂O can be enhanced if the immersion solution contains species such as noble metal ions like [PdCl₄]²⁻ which can be reduced to a lower oxidation state. It is likely that the Pd spontaneous deposition can be initialized as result of two simultaneous half-cell reactions at the Ru surface. One is a reduction of [PdCl₄]²⁻:



and the other is Ru⁰ oxidation,



The corresponding driving force for Pd deposition, ΔU , in this case would be the difference between the equilibrium potential of these two half-cell reactions, $\Delta E_{\text{Pt}/\text{PtCl}_6^{2-}} - \Delta E_{\text{Ru}^0/\text{Ru}_{\text{oxidized}}}$, assuming that reduction reaction occurs at the potentials

more positive than the potential of oxidation reaction.¹

The surface oxidation of Ru(000 1) is limited to formation of one RuOH monolayer [8,9], which would limit the amount of Pd deposited to $\frac{1}{2}$ ML, because of the difference in the number of electrons exchanged in two reactions. The intriguing fact is that a multilayer Pd deposit was formed on a Ru(000 1) surface. This indicates that either the oxidation of Ru to RuOH under these conditions is not limited to a surface monolayer, or a higher oxidation state of Ru is formed, or some third reaction takes place. However, voltammetry and in situ SXS show that the oxidation of Ru(000 1) beyond a monolayer of RuOH and the oxidative dissolution of Ru, require high potentials above 1.3 V [8,9] in sulfuric and perchloric acids. The presence of chloride can change this situation and facilitate either a deeper Ru oxidation, or even its dissolution. Further work to elucidate this question will involve tests of spontaneous deposition with other Pd salts, and thin layer cell experiments to determine the possible presence of Ru ions.

4. Conclusions

The spontaneous deposition of Pd on a Ru(000 1) surface, described in this letter, is a new phenomenon involving noble metal deposition on a noble metal substrate. Results show that Pd forms an epitaxial textured multilayer deposit whose thickness can be controlled by the amount of [PdCl₄]²⁻ available in the solution volume in contact with a Ru(000 1) surface. The investigation of the morphology of the Pd layers obtained under various deposition regimes suggests that the initial Pd growth involves a formation of one or two wetting monolayers, while further growth results in formation of a faceted Pd deposit. A local cell mechanism appears to be responsible for initial stage of spontaneous deposition of Pd on a Ru

¹ It is assumed that the reversible potential of [PdCl₄]²⁻ reduction is actual onset of Pd deposition which starts at the potentials around 0.360 V [12], while 0.05 V was taken as the potential of the Ru oxidation [8,9].

surface where Ru oxidation to RuOH is the cathodic reaction occurring on the crystal surface. In order to explain multilayer Pd deposition by this model, one has to assume multilayer RuOH formation, or a higher oxidation state of Ru.

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