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The epitaxial growth of Pd electrodeposition on Au(1 0 0) studied by LEED and RHEED

A.L.N. Pinheiro [a], M.S. Zei [a,b,*], M.F. Luo [b], G. Ertl [a]

[a] *Fritz-Haber-Institut der Max-Planck-Gesellschaft*
[b] *Department of Physics and Nanocatalyst Research Centre, National Central University, Jungli 32054, Taiwan, ROC*

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Abstract

The epitaxial growth of Pd adlayers electrochemically deposited onto Au(1 0 0) has been studied by LEED, RHEED and AES. For the first 6 ML, the Pd deposits grow pseudomorphically on Au(1 0 0) with a lateral expansion of 4.5% with respect to bulk Pd. The strain in the expanded commensurate (1×1) Pd layers on Au(1 0 0) begins to be relieved at the Pd coverage between 6 and 9 ML range by formation of a compressed Pd film with respect to Au(1 0 0) surface and the compression increases continuously with thickness. At ca. 20 ML Pd the lattice constant of the film approaches to the bulk Pd and three-dimensional Pd islands develop since around 30 ML coverage. No superstructure due to the Pd–Au surface alloy can be found for coverages from monolayer up to 30 ML Pd on Au(1 0 0). A $c(2 \times 2)$ phase has been observed on the Pd-deposited Au(1 0 0) electrodes, which is ascribed to an ordered Cl adlayers adsorbed on Pd adlayers rather than a Pd–Au surface alloy.

Keywords: Auger electron spectroscopy; Palladium; Reflection high-energy electron diffraction (RHEED); Metal-electrolyte interfaces; Cyclic voltammetry; Single crystal epitaxy

1. Introduction

Palladium is one of the most important materials because of its high catalytic activities for many chemical reactions. Pd-based alloy system draws more attention in these days. The Pd–Au system, by virtue of its intriguing catalytic properties, has been the subject of numerous studies, including direct and indirect analysis of the formation of Pd thin films and Pd–Au surface alloys for different substrate orientations [1–4]. Different properties have been observed for Pd on different Au surface orientations. For instance, monolayer Pd-covered Au(1 1 1) behaves like massive Pd(1 1 1) towards formic acid oxidation, however, monolayer Pd on Au(1 0 0) shows different catalytic properties from massive Pd(1 0 0) [5,6]. The differences of the catalytic activity of the deposited Pd layer on Au surfaces are primarily attributed to growth mode of the Pd deposits [7]. Therefore characterizing the growth mode is essential to understand and control the catalytic properties. The present study is thus devoted to furthering the understanding of the growth of Pd electrodeposited onto Au(1 0 0). We focus on characterization of structures of the Pd thin films as well as Pd–Au interface, and discuss the growth mechanism in context of interface energy and lattice mismatch [7–9] between the admetal and the substrate [10,11].

The electrodeposition of Pd onto Au(1 0 0) was previously studied by Kibler et al. [12] using in situ STM and they concluded that a surface Pd–Au alloy is formed after Pd UPD (under-potential deposition) on Au(1 0 0). A similar result has been reported for LEIS (low energy ion scattering) study of monolayer Pd coverage on Au(1 1 1) [3], in which intermixing of Pd–Au is already appreciable at 300 K. However, the results contradict with other

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[*] Corresponding author. Address: Department of Physics and Nanocatalyst Research Centre, National Central University, Jungli 32054, Taiwan, ROC. Fax: +886 3 4251175.
E-mail address: zei@phy.ncu.edu.tw (M.S. Zei).

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measurements on similar systems. Takahasi et al. [13] using surface X-ray diffraction found a pseudomorphic growth of Pd monolayer on Au(1 1 1) but did not observed intermixing between Pd and Au. Additionally, the studies of Pd/Au(1 1 1) by use of LEED, XPS, AES and STM [17,18] showed that intermixing for Pd deposition on Au(1 1 1) at room temperature is negligible, and Pd_2Au surface alloy with $(\sqrt{3} \times \sqrt{3})R30°$ structure was obtained only by pretreatment at 450 K [17]. Controversy also exists in structures of grown Pd thin films. For example, LEED measurements indicate Pd film on Au(1 0 0) in UHV grow through layer-by-layer mode up to 10 ML, and the result is rationalized by small lattice mismatch between Pd and Au (4.6%) [14]. Whilst, on Au(1 1 1) layered growth sustains only up to four layers under electrochemical conditions [5]. Consequently, a detailed determination of the surface crystallography of Pd/Au(1 0 0) is of considerable interest.

In the present work we applied reflection high energy electron diffraction (RHEED) combined with LEED and AES to study the growth of electrochemically deposited Pd onto Au(1 0 0). The Pd-deposited Au(1 0 0) electrode was rinsed with water after emersion in order to remove the coadsorbed anions on the deposited Pd layer, which may shield the bare Pd layer as has been observed by in situ STM [12]. The lateral spacing of Pd adlayer with respect of Au(1 0 0) substrate and the inter-layer distances of Pd film were determined by RHEED. The results allow us to conclude that the Pd deposits grow pseudomorphically on Au(100) up to 6 ML, beyond 6 ML the lateral spacing of the outermost layers of Pd(1 0 0) film starts to contract for strain relief, and finally three-dimensional Pd clusters develop at ca. 30 ML coverage. The growth features are significant because they have not been reported so far in an electrochemical environment. On the other hand, a c(2 × 2) superstructure was observed on Pd-covered Au(1 0 0) surfaces. The superstructure is independent of Pd coverages and ascribed to an ordered Cl adlayer on Pd layers. We compared this superstructure to the c(2 × 2) phase of surface alloys observed from other systems, including Pd/Cu(1 0 0) [19,20], Pd/Au(1 1 1) [18], Mn/Au(1 1 1) [21], Mn/Ag(1 0 0) [22] and Pd/Au(1 0 0) [14].

2. Experimental

The experiments were performed with an apparatus consisting of a UHV chamber (base pressure $<1.5 \times 10^{-10}$ mbar) incorporating LEED, RHEED and AES, an electrochemical chamber (base pressure $<1.0 \times 10^{-9}$ mbar), an electrochemical cell and a closed sample transfer. The electrochemical cell consists of two separated parts, which allows us to use a flow-cell procedure to change electrolyte solutions under-potential control and in an air-free atmosphere.

RHEED was performed with an incident electron beam (40 keV) at a grazing angle of 2–3° to the surface. The RHEED electron beam also acts as the primary electron source for AES. This combination allows us to obtain both structural and chemical information from the same surface region simultaneously.

The working electrode, a Au(1 0 0) single crystal disc of 7 mm diameter and 2 mm thickness, was mounted between tungsten wires, which also served for resistive heating of the sample. The electrode surface was prepared by cycles of argon ion bombardments (5×10^{-5} mbar, at room temperature and 700 °C) and annealing, until the sample surface was free from disorder and impurities, monitored by LEED/RHEED and AES. The sample was then transferred to the electrochemical chamber under UHV conditions. The electrolyte forms a meniscus on top of a glass capillary, through which the electrolyte is filled by pressure from argon gas and then the working electrode is brought into contact with the meniscus by movement of the glass capillary [23]. Standard electrochemical equipment was employed for potential sweeping. The experimental details have been reported elsewhere [23,24]. A platinum wire with 0.4 mm diameter was used as counter electrode in the electrolyte vessel on top of a glass capillary [23]. In order to check the cleanliness of the Au electrode the cyclic voltammogram for the clean Au(1 0 0) electrode was first recorded in a 0.1 M HCl solution prior to Pd deposition. Electrochemical deposition was performed by cycling the potential between 0.4 and +0.7 V vs. Ag/AgCl in 0.1 M H_2SO_4 + 1 mM $PdCl_4^{2-}$ + 0.7 mM HCl solution. After Pd deposition onto the Au(1 0 0) electrode (cell I) and rinsing with water (cell II) the Pd/Au(1 0 0) electrodes were transferred into UHV and characterized by LEED/RHEED and AES.

3. Results

3.1. Cyclic current-potential curve for Pd UPD on Au(100)

Prior to electrochemical experiments the Au(1 0 0) single crystal surfaces were cleaned by argon ion sputtering and annealed in UHV until the surface was well-ordered and free from impurities (monitored by LEED/RHEED (Fig. 1) and AES (Fig. 2a)). The reconstructed hexagonal overlayer on Au(1 0 0) is illustrated by the 1/5-order reflections in the diffraction patterns shown in Fig. 1, where also shows double diffraction of beams from a square substrate lattice by an hexagonal overlayer [25]. The cyclic voltammetry (CV) was conducted by immersion of the reconstructed Au(1 0 0) electrode at 0.8 V, where the reconstruction of the Au(1 0 0) surface has been lifted and the surface is covered by numerous (1 × 1)-Au islands [12]. Subsequently, the (1 × 1)-Au(1 0 0) electrode was negatively scanned for under-potential deposition of Pd onto Au(1 0 0)-(1 × 1). The CV for Pd UPD on Au(1 0 0) in 0.1 M H_2SO_4 + 0.1 mM $PdCl_4^{2-}$ + 0.7 mM HCl solution is presented in Fig. 3, showing a cathodic peak at 0.55 V and an anodic peak at 0.65 V, similar to the CV obtained from Pd UPD on Au(1 0 0)-(1 × 1) with islands in 0.1 M H_2SO_4 + 0.1 mM $PdCl_4^{2-}$ + 0.2 mM HCl solution [12]. The charge under the current peak at 0.55 V is ca. 320 μC/cm², corresponding to ca.