



## Preparation and characterization of ultra-flat single crystal surfaces of Pd(1 1 1) and Au(1 1 1) by an in situ interference optical microscopy

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### ABSTRACT

It is shown that the Pd(1 1 1) and Au(1 1 1) surfaces with wide atomically flat terraces having widths in a range of 2–10 μm can be prepared by annealing in an argon stream. These surfaces were investigated by a laser confocal microscope combined with a differential interference contrast microscope (LCM–DIM). It is remarkable that regularly aligned step lines are clearly discerned in electrolyte solutions. The step lines observed by LCM–DIM are monatomic steps confirmed by scanning tunneling microscopy and atomic force microscopy. It is expected that LCM–DIM is a new powerful in situ method for the investigation of electrochemical reactions with the capability of atomic layer resolution.

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### 1. Introduction

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) operated at electrode surfaces in electrolyte solutions are well recognized as the premier techniques for structural investigation of electrode/electrolyte interface on the atomic level [1–3]. Although these techniques have been successfully applied to reveal atomic structures of electrode surfaces in solution, observable scan areas are small, typically only a few micrometer square. This limitation makes it difficult to understand the overall aspect of electrochemical reactions taking place in the entire area of a real electrode surface. Furthermore, probes such as the tunneling tip in STM and the cantilever in AFM measurements may interfere with electrochemical processes. It is evident particularly in the case of electrodeposition that the tunneling tip disturbs the deposition and diffusion processes of metal ions [4–6].

Although the conventional optical interference microscope has been widely employed to observe steps, Sazaki's group reported for the first time that the elementary growth steps (5.6 nm in height) on the {1 1 0} surfaces of a tetragonal lysozyme crystal in aqueous solutions can be seen by a laser confocal microscope combined with a differential interference contrast microscope (LCM–DIM) [7,8]. We have long been interested in developing an

optical microscopic technique for the evaluation of electrochemical reactions on an atomic level, because of the fact that the observable area is very large (more than 100 μm square) compared with that of STM and AFM. It is also noteworthy that the acquisition time of each image in LCM–DIM is very short, typically a few second [7,8], compared with those in STM and AFM.

However, for the purpose of observing monatomic steps on metal surfaces in electrochemical environment, the vertical resolution must be increased by an order of magnitude, because the height of monatomic steps of commonly interested metals is less than 0.3 nm. We have recently demonstrated that monatomic steps with a height of 0.25 nm on ultra-flat Au(1 1 1) surfaces are clearly discerned in electrolyte solutions and the anodic dissolution of Au in an acid solution containing chloride ions can be followed by our LCM–DIM [9,10].

Such results prompted us to try to prepare ultra-flat Pd(1 1 1) surfaces. We have previously reported that the anodic dissolution at iodine modified-Pd(1 1 1) occurs exclusively at step edges in a layer-by-layer sequence without deterioration of the iodine adlattice structure [11,12]. It is important to note that a very flat Pd surfaces having terrace widths greater than several micrometers is needed for the evaluation of the anodic dissolution, because the lateral resolution of the LCM–DIM method is limited by the wave-length of light as in the conventional optical microscopy.

In this paper, therefore, we describe the surface structures of Pd(1 1 1) and Au(1 1 1) after annealing in a furnace in a temperature range of 800–1200 °C for several hours under purified argon atmosphere in order to increase the terrace width. It is shown that

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the step lines observed on Pd(1 1 1) and Au(1 1 1) by LCM–DIM in aqueous solutions truly correspond to monatomic steps. It is concluded that LCM–DIM is a new powerful in situ method for the investigation of electrochemical reactions with the capability of atomic layer resolution.

## 2. Experimental setup and procedure

The apparatus of our LCM–DIM was constructed based on an optical system (FV300, Olympus Optical Co. Ltd.) with a superluminescent diode (Amonics Ltd.) to eliminate interference fringes.

This set up has been described in details by Sazaki's group [7,8]. In our apparatus, the polarizer and analyzer based on Ag nano-particles (CODIXX Germany: ColorPol®VIS 600 BC4) have been used in order to resolve single atomic steps on Au(1 1 1). A more detailed experimental setup will be described elsewhere [10].

Spherical single crystal beads of Pd and Au were obtained by melting the end of each wire (99.999% purity, 0.8 mm diameter) in a H<sub>2</sub>/O<sub>2</sub> flame as described previously [11,13–15]. The Pd and Au single crystal spheres consist of eight facets of (1 1 1) in an octahedral configuration. One of the facets was directly taken under investigation. In this study, the single crystal beads were further annealed in an electro-magnetic furnace (HOTSHOT5, Ambrell Ltd.) in a temperature range of 800–1200 °C under purified argon atmosphere in order to increase the terrace width. The ultra-pure argon gas was further purified by an intelligent gas purifier (IGP-200i, Servomex Ltd.).

Final treatment of the clean and ordered surfaces consisted of flame annealing, slow cooling (in a stream of high purity inert Argon gas), and immersion in ultra-pure water (to prevent environmental contamination). All solutions were prepared from H<sub>2</sub>SO<sub>4</sub> (Merck, Suprapure grade) and Milli-Q Plus water (Millipore Systems). Potentials were referenced against the reversible hydrogen electrode (RHE).

## 3. Results and discussion

### 3.1. Ultra-flat Pd(1 1 1)

Although we have previously shown that naturally grown (1 1 1) facets of Pd [11–13], Au [14], and Pt [15] on single crystal beads formed at each end of their respective metal wires can be characterized by atomically flat terrace-step structures, the width of atomically flat terraces are usually in the range of 50–300 nm.

Fig. 1 shows an example of STM image (100 × 100 nm<sup>2</sup>) of a conventionally prepared Pd(1 1 1) facet in a 0.1 M sulfuric acid solution. Monatomic steps are seen to run nearly parallel or at an angle of ca. 60° to each other, as expected for surfaces with a three-fold symmetry, in an agreement with the previous results [11–13,16]. However, it is clear that the width of terraces is less than 100 nm.

For LCM–DIM experiments, it is necessary to prepare a very flat Pd(1 1 1) surface, having terrace widths greater than several micrometers, because the lateral resolution of the LCM–DIM method is limited by the wave-length of light as in the conventional optical microscopy as described above.

After characterization of the surface morphology by STM or AFM, we found for the first time that the surface of Pd(1 1 1) has very wide atomically flat terraces having widths in a range of 2–20 μm. Those ultra-flat Pd(1 1 1) surfaces were subjected to an examination by LCM–DIM.

Fig. 2A shows a typical LCM–DIM image of Pd(1 1 1) acquired in an area of 70 × 70 μm<sup>2</sup> in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Note that the acquisition time of the image was only 2 s. It is remarkable that regularly aligned step lines are clearly discerned. A pyramidal structure

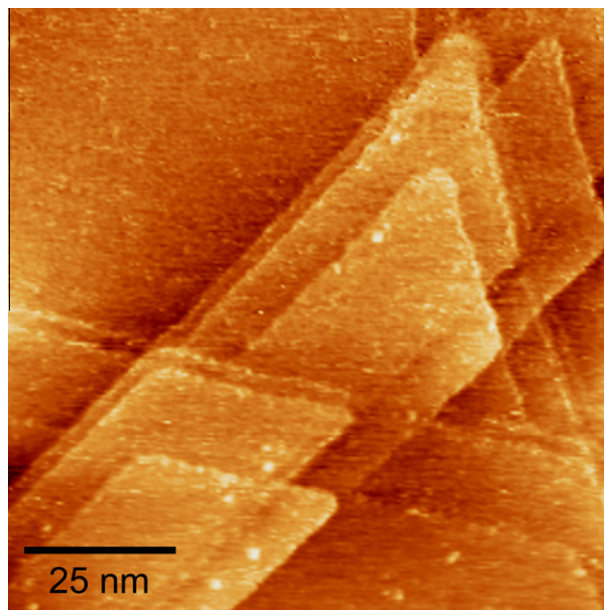


Fig. 1. An STM image of Pd(1 1 1) of a 100 × 100 nm<sup>2</sup> area in a 0.1 M H<sub>2</sub>SO<sub>4</sub> solution. The electrode potential was 0.8 V vs. RHE. Tunneling current was 1 nA.

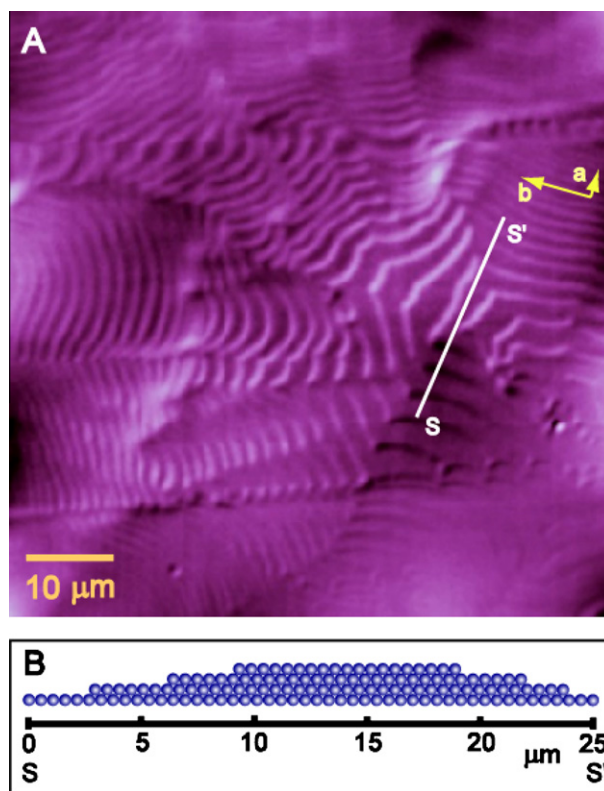


Fig. 2. (A) A typical LCM–DIM image of an ultra-flat Pd(1 1 1) surface in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution. The electrode potential was 0.8 V vs. RHE. (B) A model structure along the line (S–S') in (A).

can be seen over the entire region in the area of 70 × 70 μm<sup>2</sup>. It is surprisingly found that terrace widths in the directions indicated by arrow (a) and arrow (b) are in the range of 2–5 μm and greater than 10–20 μm, respectively as shown in Fig. 2A. To confirm that the step lines observed by LCM–DIM are all mono-atomic steps,

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