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In situ, real-time monitoring of electrode surfaces by scanning tunneling microscopy. III. Surface structure of Pt and Pd electrodes

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Pt and Pd electrodes were monitored by STM *in situ* in real time. In the case of Cu deposition on Pd, small domains of Cu were first formed and they gradually merged to form terraces. The surface finally became relatively smooth. Surface structure change of Pt electrode during oxide formation/reduction was also investigated. Growth of parallel ridge and domelike structures was observed.

I. INTRODUCTION

It is well recognized that the structure of electrode surfaces has a significant effect on the reactivity of the electrode. Not only the real surface area for the reaction is increased by the roughness of the electrode but also the microstructure of the surface is strongly correlated with the number and the distribution of the active sites. Moreover, the surface structure of the electrode often changes during the electrochemical reaction caused by adsorption/desorption of metal atoms or even by formation/reduction of oxide layer.

To understand the effect of surface structure on the reactivity of the electrode, it is essential to monitor the surface structure of the electrode with high resolution (atomic to μm scale). The presence of an electrolyte solution in electrochemical systems inhibits the extensive use of surface analysis tools such LEED, most of which can be used only under ultrahigh vacuum (UHV) conditions. Furthermore, most of the techniques have relatively low resolution both laterally and vertically. Scanning tunneling microscope (STM) which has been developed significantly within last few years

is most suited for this purpose.¹ A real space image of conductive surface can be obtained relatively easily with very high resolution in various media including electrolyte solutions. To apply STM to electrochemical situation, however, special care must be taken. Apart from the sample and the tip, which are needed for usual STM measurements in vacuum or in air, it is necessary to add extra two electrodes to the system. A reference electrode is required as a reference potential point and a counterelectrode to carry electrochemical current which flows at the sample (working electrode). In the electrochemical STM measurement, not only the bias between the sample and the tip but also the potential of the sample with respect to the reference electrode should be controlled. In fact, the potential of the sample and the tip are set independently with respect to the reference electrode. Various groups have reported the construction of STM systems for electrochemical study.²⁻¹⁰ We have also constructed an STM system for electrochemical application based on a commercially available STM with a homebuilt potentiostat and applied the system for the study of Cu deposition on Pt.¹¹ With our system, we can follow the dynamics of surface

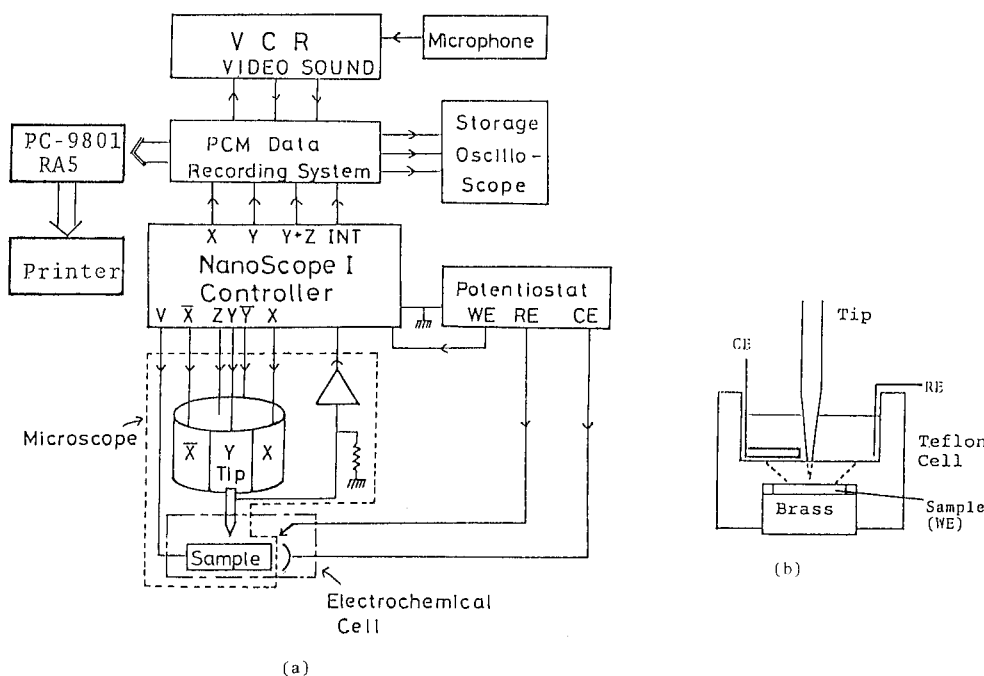


FIG. 1. Block diagram of the present STM system.

structure change during electrochemical reactions.

In this article, we continued further the study of *in situ*, real time monitoring of electrode surfaces. The systems investigated in this study are Cu deposition on Pd electrode and surface structure change of Pt during the formation/reduction of oxide layer.

II. STM SYSTEM FOR ELECTROCHEMICAL STUDY

A block diagram of the present STM system is shown in Fig. 1(a). A STM used in this study was a NanoScope I of Digital Instruments (CA, U.S.A.). A homebuilt potentiostat was added to the system to control the potential of the tip and a sample with respect to a reference electrode and carry

out electrochemical reactions. A potential control circuitry of the system is essentially of a well known four electrode potentiostat (bipotentiostat) commonly used for a rotating ring disk electrode and was presented before.¹¹ A Pt wire and a Pt foil were used as a reference electrode (RE) and a counter electrode (CE), respectively. The working electrode (WE) output of the potentiostat is connected to the external bias input of the NanoScope I which is connected to the base of the microscope on which an electrochemical cell [Fig. 1(b)] is placed. The ground of the potentiostat and that of the control unit of NanoScope I are connected. A PCM data recording system (NF Electronics, RP-880) with a VCR is employed for continuous data recording. More

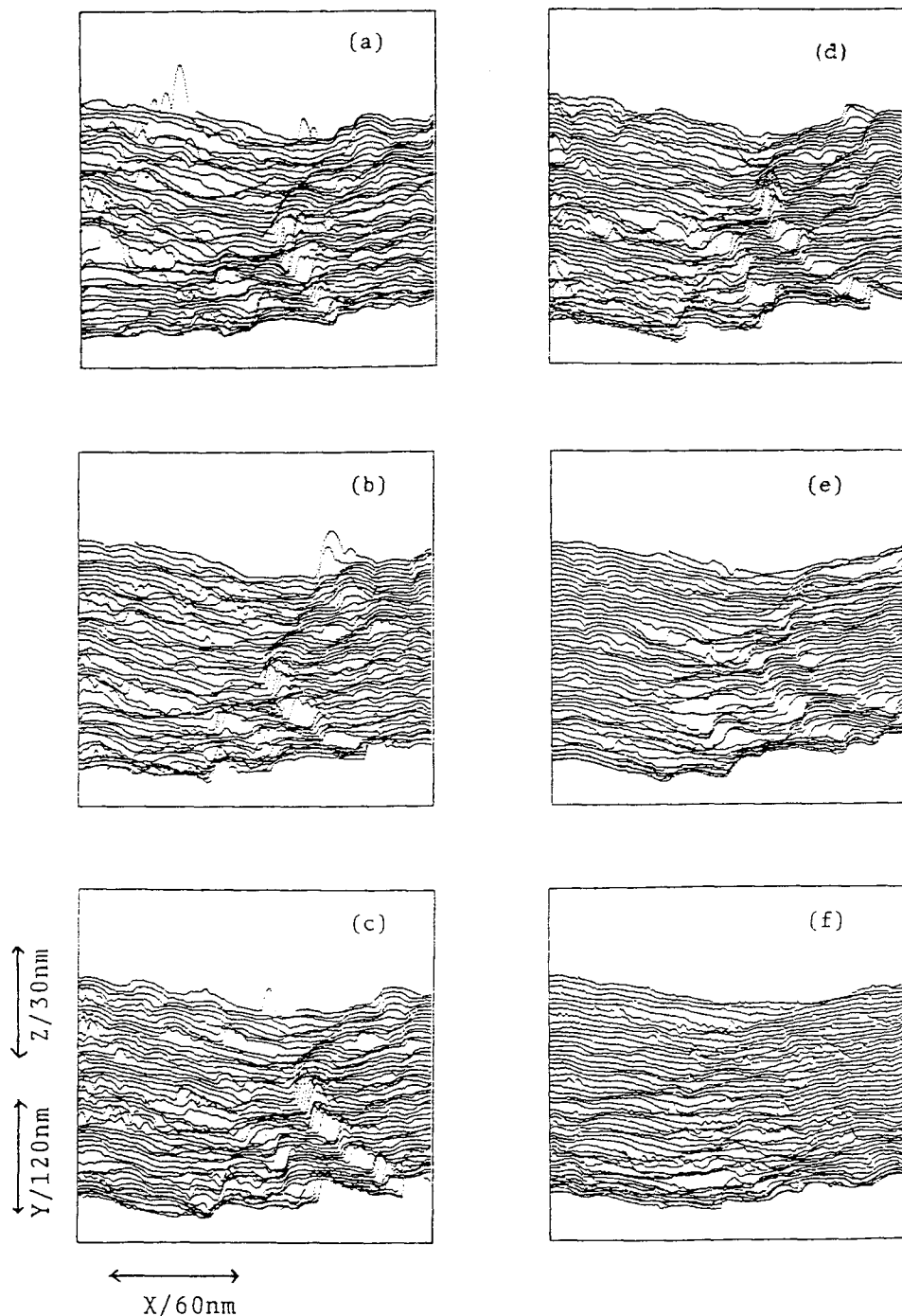


FIG. 2. STM images of Pd electrode surface obtained during Cu deposition in 2 mM HClO_4 + 5 mM CuSO_4 . Electrode potential of Pd: 0 V vs Pt. Current: $-10 \mu\text{A}/\text{cm}^2$. Tip potential: +700 mV vs Pt. (a) 8 s, (b) 30 s, (c) 45 s, (d) 83 s, (e) 98 s, and (f) 118 s after the potential was applied.

than 1 G byte of information can be stored on a 2 h tape (cf. an ordinary 2HD floppy disk has storing capacity of 1M byte). Thus, by using this system, vast amounts of information can be stored very economically. This system has a digital output for further data processing by a computer (NEC, 32 bit, PC9801 RA5 with 40 M byte hard disk system). Turbo C was used for the main program but the data transfer routine was written in machine code. Played-back STM images can be monitored by using a storage oscilloscope and obtained as hard copy of CRT images of the computer.

Tunneling tips employed are Pt(90%)–Ir(10%) of Longreach Scientific Resources (Maine, U.S.A.), ($\phi = 0.25$

mm) coated with soft glass or epoxy resin except at the very tip ($\sim 5 \mu\text{m}$).

III. RESULTS AND DISCUSSION

A. Cu deposition on Pd

Metal deposition is one of the most important electrochemical processes both fundamentally and practically. There have been many publications concerning how deposition proceeds and how the electrochemical conditions affect the structure of the deposits. Thus, it is natural to try to investigate the electrochemical metal deposition by STM.

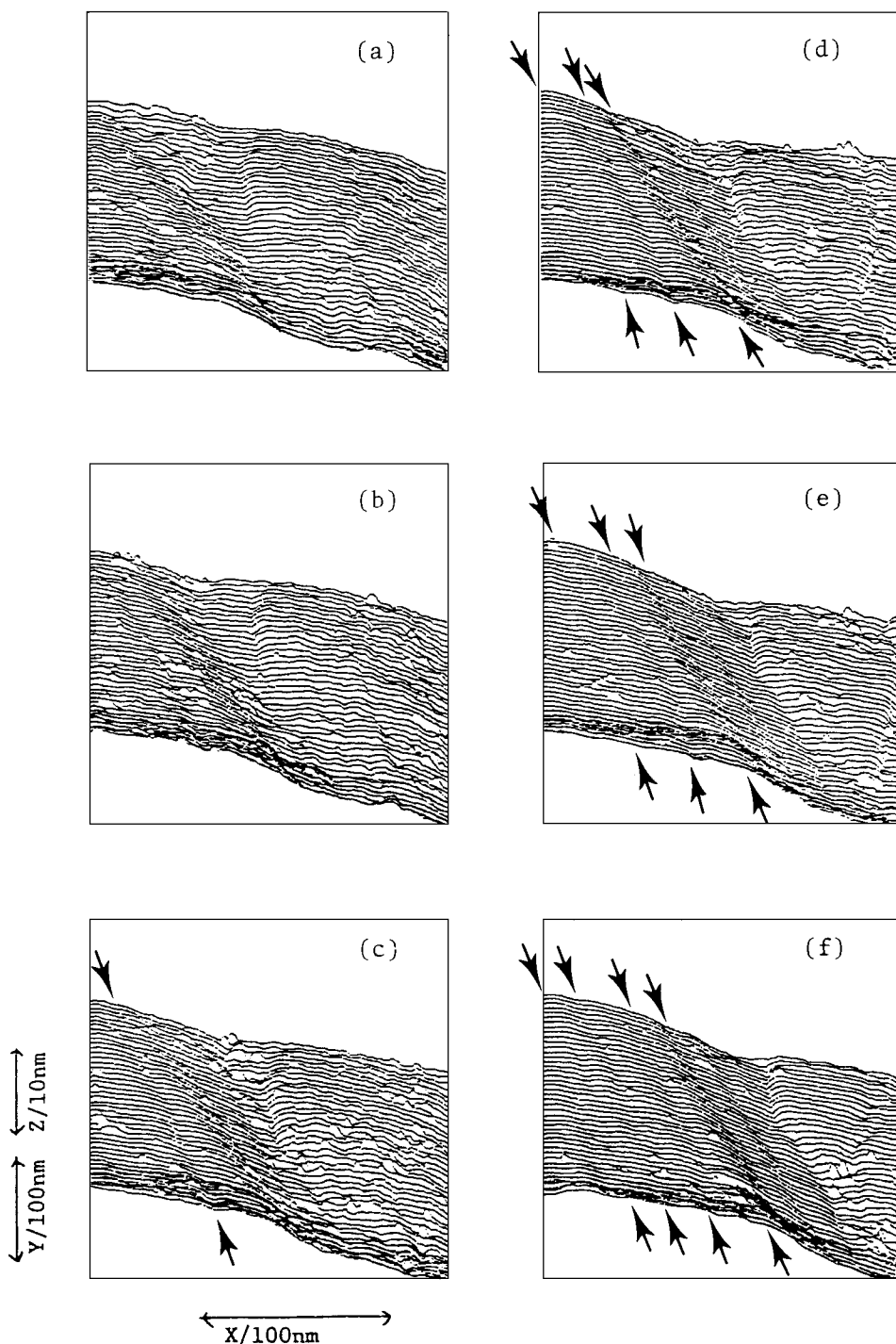


FIG. 3. STM images of Pt surface (a) 45 s, (b) 2 min 26 s, (c) 2 min 56 s, (d) 4 min 56 s, (e) 11 min 15 s, and (f) 15 min 19 s after potential was pulsed from +950 to -350 mV in 2 mM HClO_4 .

We have successfully followed Cu deposition on Pt by STM as mentioned before.¹¹ Recently, several electrochemical studies on underpotential deposition (UPD) of Cu on Pd were published.^{12,13} Before studying UPD of Cu on Pd, we investigated the bulk deposition of Cu on Pd by STM. Figure 2 shows the real time deposition of Pd during Cu deposition in 2 mM HClO₄ + 5 mM CuSO₄ at 0 V vs Pt obtained *in situ*. To avoid the Cu deposition on the tip, the tip potential was kept at +700 mV vs Pt. At the initial stage [Figs.

2(a) and 2(b)], rather noisy images were obtained and small domains, possibly of Cu, were observed. The domains grew laterally with time and merged to form terraces as shown in Figs. 2(c) and 2(d). Further deposition seemed to occur preferentially at step portion [Fig. 2(e)] and the surface finally became relatively smooth [Fig. 2(f)]. STM images became stable as deposition proceeded. We can speculate that the noisy portion is the place where preferential deposition is taking place.

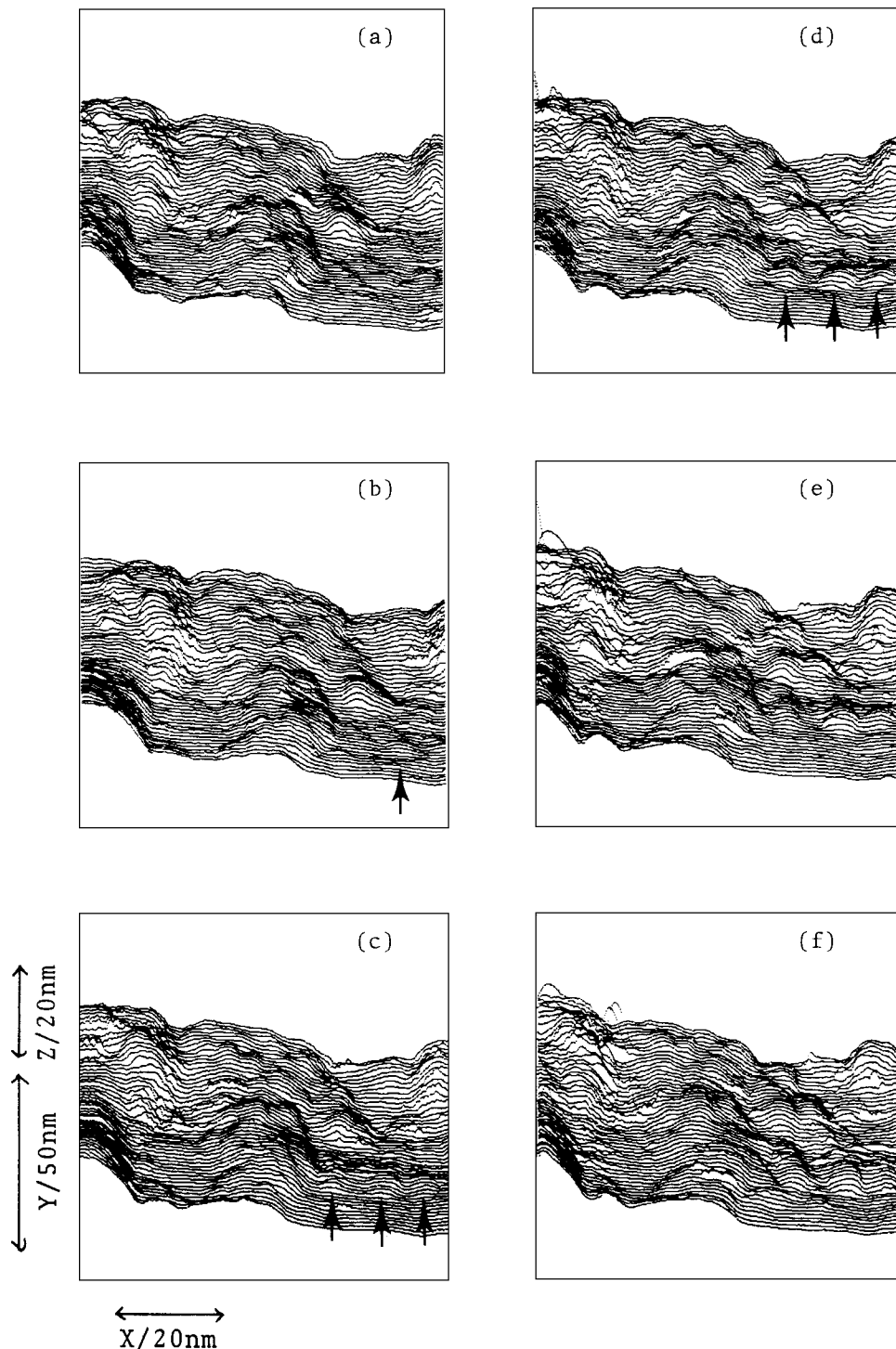


FIG. 4. STM images of Pt surface (a) 8 min 21 s, (b) 8 min 50 s, (c) 9 min 10 s, (d) 9 min 20 s, (e) 9 min 30 s, and (f) 9 min 40 s after potential was pulsed from +1.5 V vs Pt to -1.1 V vs Pt.

B. Structure change of Pt surface by formation/reduction of oxide

Surface structure change of noble metal electrodes due to potential cycles have been pointed out and several STM studies have been reported.¹⁴⁻¹⁶ Although *in situ* STM investigation of this process has been carried out,¹⁶ no report of *in situ*, real time monitoring of the surface structure change by STM is available. Figure 3 shows STM images of polycrystalline Pt surface in 2 mM HClO₄ solution when the potential was first pulsed to +950 mV vs Pt at which Pt oxide layer was formed and then pulsed to -350 mV vs Pt to reduce the oxide layer. The potential of the Pt electrode and the tip were kept at -350 mV vs Pt and +550 mV vs Pt, respectively, during STM imaging. There seemed to exist two large domains which merge at the middle of the image. The domains on the left-hand side had a steep slope and the one on the right-hand portion was relatively flat [Fig. 3(a)]. At the beginning, the left hand-portion had a featureless surface and there was a terrace surrounded by sharp steps in the flat area of the right-hand portion. As time passed, parallel ridge structures with steps of mono to several atomic heights became visible at the left-hand portion as pointed out by arrows [Figs. 3(c)-3(f)]. Separation of these terraces are ~20 nm. These results are quite similar to those of Itaya *et al.* obtained in H₂SO₄ solution,¹⁶ although they did not monitor the surface continuously. We must stress that the STM images reported here were obtained *in situ*, in real time, i.e., the tip was never retracted. It should be also noted here that the resolution of the present system is quite high. Figure 4 shows STM images of Pt taken in a separate experiment but in the same solution. The potential of the Pt electrode was first kept at +1.5 V vs Pt. Even oxygen gas bubble evolving from the Pt surface was clearly observed at this potential. The potential was then pulsed to -1.5 V vs Pt at which reduction of oxide layer should occur. All the STM images shown in Fig. 4 were obtained at this potential. No clear change was observed within this region during the first 8 min after the potential pulse. However, as shown in Fig. 4(b), a small cluster started to grow after 8 min 50 s at the flat portion seen in the front-right part of the image as indicated by an arrow. Once this change had started, relatively quick structure change was observed in this region. The cluster became three parallel rows within 20 s [Fig. 4(c)-4(e)] and finally a domelike structure became dominant in the flat region [Fig. 4(f)]. Of course, this result does not mean that

nothing happened at the surface during the first 8 min. Some change might take place at other part of the surface where STM images has not been recorded. These STM images (Figs 3 and Fig. 4) show that the surface structure change in the electrochemical situation occurs with quite a long time constant. It is interesting to note that Vazquez *et al.* examined Pt surface *ex situ* by STM after potential cycles and found both parallel ridge and domelike structures.¹⁵ Although it is not yet clear why these structures developed but it is demonstrated in this paper that *in situ*, real time monitoring electrode surface certainly provides useful information how these structures grow and with more investigations we expect to find eventually the answer why a certain structure grows at a given point.

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