In Situ Electrochemical AFM Observation for Dissolution of Plated Copper in Aqueous Solution

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Atomic Force Microscopy (AFM) is a powerful tool to investigate topographical information about materials' surfaces on nano-scale. In this study, we observed electrochemical dissolution processes of plated copper *in situ* by electrochemical AFM (EC-AFM) in aqueous solutions. The potentials of specimens were regulated to a certain value during the observations and the surface topographical images were captured by EC-AFM intermittently. The series of observation made it possible for us to get the new information and concrete images of the dissolution on nano- or submicron scale.

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1. INTRODUCTION

Nanotechnology in electroplating processes has received a growing attention because of the broad field of potential applications [1]. Especially, several investigations have been conducted in nanostructured materials produced by electrochemical procedures, and a lot of interesting results from both fundamental and practical viewpoints have been obtained in resent years [1-5]. In order to raise worldwide concern about nanotechnology in electroplating much more, not only production techniques but also characterization techniques in electroplating processes on a nano-scale are very important. Electrochemical atomic force microscopy (EC-AFM) is one of the powerful tools to observe the electrochemical behavior on electrode surface *in-situ* in electrochemical environment [6-15]. *In-situ* EC-AFM studies on an atomic scale tell us infinite possibility of electrochemical processes, however, those on a nano- or submicron scale give us practically useful information[16]. Therefore, we have been investigated the pulse plating by EC-AFM in the previous paper, and have concluded that EC-AFM could be utilized for *in-situ* analysis of pulse plating. In this paper, the preliminary study of *in-situ* EC-AFM investigation for dissolution of plated copper on iron sheet.

2. EXPERIMENTAL

Figure 1 shows a schematic illustration of EC-AFM system. The system is consist of EC-AFM cell, AFM control unit (Pico SPM; Molecular Imaging), and current-potential control unit(HZ-3000; Hokuto Denko Co.). Figure 2 shows a schematic illustration of cross section of EC-AFM cell. The sample observed was plated copper on iron sheet cut into 20 × 20 mm (0.787 × 0.787 in.). The EC-AFM cell was composed of the sample as a working electrode, a platinum wire as a counter electrode, a mercury/ mercury sulfate electrode as a reference electrode, and a commercial Si_3S_4 cantilever for contact mode as an AFM cantilever. The electrolyte used was a 5 kmol m^{-3} H_2SO_4 aqueous solution, which was prepared from sulfuric acid and ultrapure water (> 18MΩ in the electric resistance, Milli-Q labo). After pouring the electrolyte into EC-AFM, constant cathodic current of 0.5mA cm^{-2} was applied and simultaneously surface topographical images (deflection mode) of the sample were captured every 56 sec. by EC-AFM. The EC-AFM was conducted under contact mode and the observation area was 2 μm × 2 μm (7.87×10^{-4} in. × 7.87×10^{-4} in.). The experiment was performed at room temperature.

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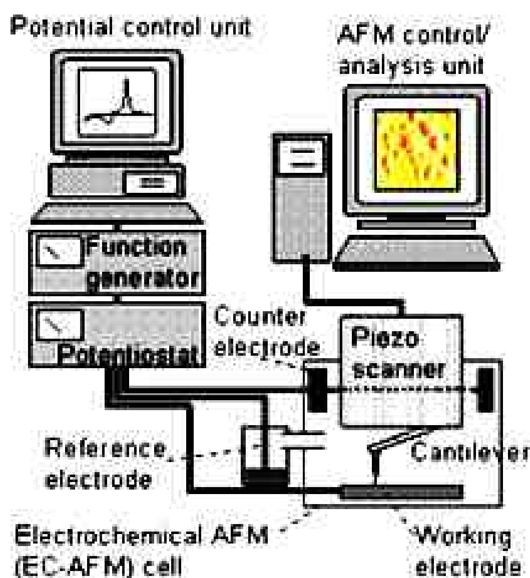

Fig. 1 Schematic illustration of EC-AFM system

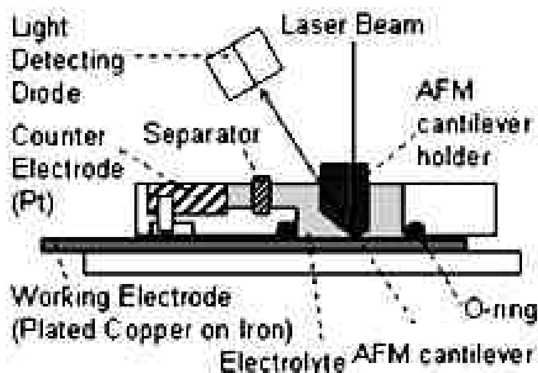

Fig. 2 Schematic illustration of cross section of EC-AFM cell

3. RESULTS AND DISCUSSION

Figure 3 shows a series of *in-situ* EC-AFM images of the sample surface in electrolyte under constant cathodic current of 0.5mA cm^{-2}, indicating the dissolution of plated copper. The images slightly drifted in the direction of left accompanied with time. Fig. 3(a) shows the plated copper consists of plenty of grains with submicron diameter. From figs. 3(a)-(e), the surface of the sample becomes more flat and the grain boundary becomes less clear when the cathodic dissolution proceeds.

The obtained results here are quite primitive, however, it is obvious that EC-AFM on a submicron scale can be applied to dynamic observation for electrochemical dissolution of the film produced by electroplating processes, as well as for electrodeposition. In the near future, we will try to investigate the electrochemical dissolution processes on a “real” nano-scale.

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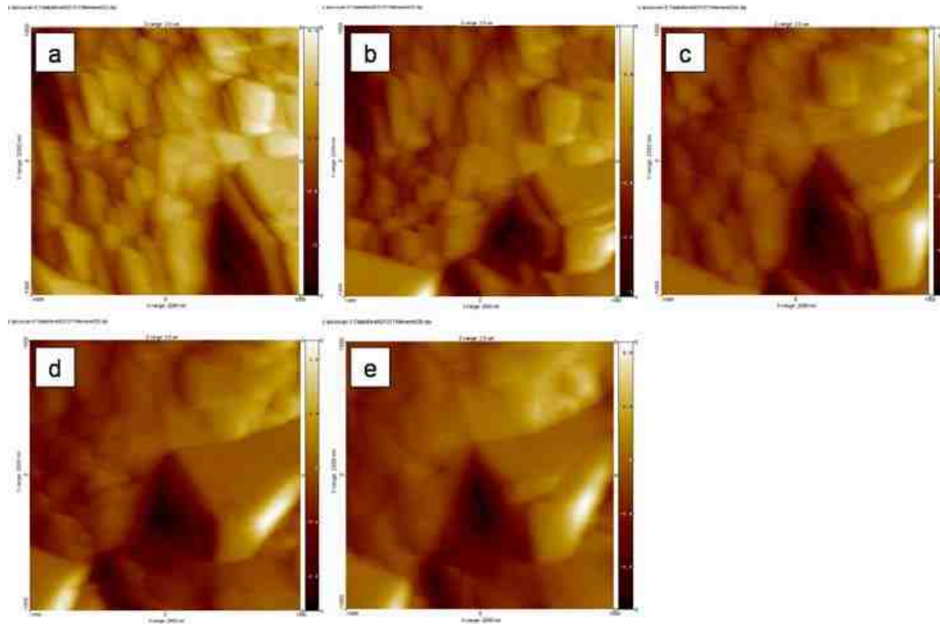

Fig.3 Series of in-situ EC-AFM images (2μm×2μm) under constant cathodic current of 0.5 mA cm^{-2}, showing dissolution of plated copper on iron.
(a) Immediately before the cathodic polarization
(b) 56 sec. after image (a)
(c) 56 sec. after image (b)
(d) 56 sec. after image (c)
(e) 56 sec. after image (d)

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