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Effects of probe downforce and bias voltage on electrochemical atomic force microscopy nanomachining of copper materials

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Abstract. This study applied electrochemical atomic force microscopy in a liquid environment. Copper was used to conduct an experiment involving nanoscale electrochemically assisted machining. Experimental conditions (e.g., number of scans, bias voltage, and electrolyte formula) were adjusted to explore the resulting phenomena and effects on nanoscale electrochemically assisted machining. The experiments showed that increasing downforce in air did not significantly influence the Cu specimen. In 0.01M phosphoric acid, applying a small amount of downforce and bias voltage resulted in a significant machining outcome. Optimal machining efficiency was achieved in the presence of both 0.01M H₃PO₄ and bias voltage of 0.5 V. Moreover, after machining, a small amount of oxide was scraped off the Cu surface and adhered to the probe.

1. Introduction

The atomic force microscope (AFM) was invented by Binnig et al. [1] in 1986. It is an improved version of the scanning tunneling microscope, which is limited by its requirement of conductive materials. The AFM overcomes the shortfall of the scanning tunneling microscope in that research materials are no longer confined to conductive materials. AFMs can be used to measure the morphology of conductive surfaces and examine the surface morphology of nonconductive materials. The AFM not only yields images with high spatial resolution but it can also operate in a vacuum, making it an indispensable instrument in the development of nanotechnologies.

Nanomachining can be achieved using ultraprecision machinery and novel technologies such as femtosecond lasers and focused ion beams. Because AFMs can operate with a variety of material surfaces and in a vacuum or atmospheric or aqueous environments, they expand research applicable to scanning probe microscopy. Therefore, the AFM is considered an effective tool for the study of nanoscale phenomena.

Electrochemical scanning probe microscopy (ECSPM) combining an electrochemical device and a scanning probe microscope was developed in 1987. ECSPM can instantly image the structural and morphological changes of material surfaces at the nanoscale during an electrochemical reaction. Therefore, ECSPM is frequently employed for this purpose.

Mudali and Katada [2] classified the application of ECSPM into five major areas of research: (1) studying the electrochemical reaction mechanism of monocristalline metal electrodes (Pt, Au, Rh, Ag,
Cu) and observation of atomic images of chemisorbed layers; (2) electrodeposition and reconstruction of electrode surface atoms under different electrode potential conditions; (3) electrochemical etching of semiconductor materials and electrodeposition of various semiconductor films; (4) bulk electroplating, batteries, conductive polymers, corrosion sensors, studying passivation mechanisms, studying corrosion, and electrochemical surface modification; and (5) nanoetching, nanodeposition, electropolishing, and anode machining.

In 1994, Rynders et al. [3] integrated a commercial-use potentiostat and Nanoscope II AFM (Digital Instruments, USA) into an electrochemical AFM (ECAFM) to examine localized corrosion near inclusions in aluminum (Al) alloy and 304 stainless steel immersed in NaCl solution. Li and Lampner [4] employed an ECAFM to examine the pitting corrosion of copper (Cu) films in NaHCO3 solution in initial stages. Williford et al. [5] adopted this equipment to observe the early stages of pitting corrosion in 304 stainless steel and grain boundary corrosion.

Lee et al. [6] adopted an ECAFM to directly examine the corrosion of 420 stainless steel in 0.001M NaCl solution at room temperature. Their surface morphology images of stainless steel showed that the specimen surface presented increasing roughness as the duration of immersion and corrosion increased. Passive films on the specimen surface were also ruptured from corrosion. Pits of varying sizes, from tens to hundreds of nanometers, on the specimen surface were also completely observed.

The vigorous development of semiconductor process technologies and miniature elements has contributed to a rapid increase in the areal density of elements and increasingly refined interconnects between two elements. Refined wires result in a high level of impedance, and a thin wire is characterized by a high level of parasitic capacitance, which severely delays signal transmission. When the refining of wires becomes unavoidable, the most effective way to improve signal delays is to select low-κ materials and replace conventional Al wires with Cu wires, which are more conductive than Al wires. Cu materials are thus considered a key component of semiconductors. Therefore, the wide range of properties of Cu materials at the nanoscale warrants in-depth investigation.

This study adopted an ECAFM to conduct nanoscale electrochemically assisted machining (NECAM) in a liquid environment. Pure Cu was used as the specimen, and nanoscale and sputtered Cu materials were subject to AFM-assisted machining under different environmental conditions. Bias voltage was applied to conduct NECAM, and the outcomes were subsequently investigated.

2. Experimental Planning and Methods

2.1. Experimental Planning

When receiving the paper, we assume that the corresponding authors grant us the copyright to use the paper for the book or journal in question. Should authors use tables or figures from other Publications, they must ask the corresponding publishers to grant them the right to publish this material in their paper. The effects of different experimental conditions on the NECAM of pure Cu specimens in a liquid environment were explored. Three environments were used for comparison: (1) In Air (2) In 0.01M H3PO4 (3) In 0.01M H3PO4 + 0.5 V bias

A contact-mode ECAFM (Nanoscope E, Digital Instruments) equipped with a potentiostat was adopted. Fig. 1 shows an image of this instrument. A glass-made liquid tank (volume = 150 mm³) was used. A silicon rubber O-ring was placed between the specimen and liquid tank to facilitate contact with the aqueous solution used in the experiment. The contact area between the specimen surface and aqueous solution was 56 mm². A platinum wire 0.3 mm in diameter was used as the reference and assisted electrode, as shown in Fig. 2.

2.2. Experimental Procedures

2.2.1 Specimen Pretreatment. In this experiment, a commercially available 99.9% Cu block was used. A wire-cutting machine was used to cut the Cu blocks into 2-mm-thick round sheets. Next, a grinder was used to grind and flatten the surface of the Cu specimen according to the particle size of aluminum oxide powder (1.0, 0.3, and 0.05 μm), creating a surface with an average roughness (Ra) of 5.7 nm. Subsequently, the specimen was immersed in alcohol and sonicated for approximately 2 minutes before it was oven-dried for use.
2.2.2 **Probe Preparation.** An OTR-8 triangular cantilever probe was used in this experiment. The morphology of the probe was observed under a scanning electron microscope, as shown in Fig. 3.

![Figure 1. Contact-mode ECAFM](image1)

(a) Schematic of liquid tank  (b) Photograph of actual model

**Figure 2.** Schematic of liquid tank and actual model used with ECAFM

![Fig. 3. OTR-8 triangular cantilever probe](image2)

2.3. **Experimental Process for NECAM**

The experimental process for NECAM in three voltage environments (air, 0.01M H₃PO₄, and 0.01M H₃PO₄) is described as follows:

**Step 1:** Scan a 5 μm × 5 μm image of the initial stage of the specimen surface under each environmental condition, as shown in Fig. 4(a).

**Step 2:** Allocate different setpoint values (i.e., downforce of 0.4, 0.8, 1.2 V) to a 2 μm × 2 μm scan area for each environmental condition, as illustrated in Fig. 4(b).

**Step 3:** After each surface is subject to different setpoints and environmental conditions, scan four 5μm × 5μm surface images for each environmental condition and observe changes in depth and surface roughness. A schematic is shown in Fig. 4(c).

![Figure 4. Perform the experimental processes of NECAM:](image3)

(a) 5μm × 5 μm scan image of initial stage of surface; (b) 2μm × 2μm processed area; and (c) 5μm × 5μm scan image (including processed area)

3. **Results and Discussion**

3.1. **Observation of Surface Nanoscale Phenomena of Pure Cu in Air**

Pure Cu was subject to downforces of 0.4, 0.8, and 1.2 V in air. Fig. 5 shows the 3D surface morphology in the initial stage. Ra and Rmax measured 1.983 and 1.388 nm, respectively.
Figs. 6–8 present the surface morphologies of the nanomachining-processed specimens, which showed no obvious signs of machining in the processed area in the center, suggesting NECAM was inefficient.

The Ra and Rmax values for the fourth machining attempt (Figs. 6–8) are listed in Table 1 and plotted in Figs. 9 and 10. The figures show that when the specimen was processed in air, the downforce and number of machining attempts increased, and Ra and Rmax values did not change considerably. However, traces of oxide formation were found in the unprocessed area on the Cu surface.

**Table 1.** Ra and Rmax depth values of pure Cu under three levels of downforce in air.

| Setpoint | Ra(nm) | Rmax(nm) |
|----------|--------|----------|
| 0.4v     | 1.604  | 28.397   |
| 0.8v     | 1.921  | 42.262   |
| 1.2v     | 2.044  | 42.563   |
3.2. Observation of Surface Nanoscale Phenomena of Pure Cu in 0.01M H₃PO₄

Pure Cu was subject to downforces of 0.4, 0.8, and 1.2 V in 0.01M H₃PO₄. Figs. 11–13 present the resulting surface following NECAM; vague signs of machining were found in the processed area, and the processed part was slightly flattened. Following reaction with phosphoric acid, products on the surface changed considerably.

The Ra and Rmax values for the fourth machining attempt (Figs. 11–13) are compiled in Table 2 and plotted in Figs. 14 and 15. The figures show that when the specimen was processed in 0.01M H₃PO₄, downforce and number of machining attempts increased, and Ra and Rmax values exhibited an increasing trend.
Table 2. Comparison of Ra and Rmax values of pure Cu under three levels of downforce in 0.01M H₃PO₄

| Setpoint | Ra(nm)  | Rmax(nm) |
|----------|---------|----------|
| 0.4v     | 3.506   | 58.633   |
| 0.8v     | 4.053   | 73.310   |
| 1.2v     | 5.643   | 94.429   |

3.3. Observation of Surface Nanoscale Phenomena of Pure Cu in an Environment of 0.01M H₃PO₄ + 0.5 V

Fig. 16 presents the initial 3D images of pure Cu processed in 0.01M H3PO4 solution and a bias voltage of 0.5 V. Ra and Rmax were measured as 14.131 and 188.157 nm, respectively.

Pure Cu was subject to downforces of 0.4, 0.8, and 1.2 V in 0.01M H3PO4 solution and a bias voltage of 0.5 V. Figs. 17–19 present the surface resulting from NECAM. The diagrams show that applying a bias voltage of 0.5 V and varying the downforce resulted in a considerable localized change in the 2 × 2-μm² processed area compared with the surrounding areas.

The Ra and Rmax values for the fourth machining attempt obtained from Figs. 17–19 are tabulated in Table 3 and plotted into Figs. 20 and 21. The results show that with 0.01M H₃PO₄ solution and a bias voltage of 0.5 V, the surface initially flattened because of the corrosive effect of the solution, causing a reduction in Ra. As the downforce and number of machining attempts increased, the processed surface began oxidizing vigorously, leading to a dramatic increase in Ra and Rmax.

Figure 16. Initial 3D images of pure Cu in an environment of 0.01M H₃PO₄ + 0.5 V

Figure 17. Three-dimensional images of pure Cu processed with 0.4 V in 0.01M H₃PO₄ + 0.5 V after (a) attempt 1, (b) attempt 2, (c) attempt 3, and (d) attempt 4

Figure 18. Three-dimensional images of pure Cu processed with 0.8 V in 0.01M H₃PO₄ + 0.5 V after (a) attempt 1, (b) attempt 2, (c) attempt 3, and (d) attempt 4

Figure 19. Three-dimensional images of pure Cu processed with 1.2 V in 0.01M H₃PO₄ + 0.5 V after (a) attempt 1, (b) attempt 2, (c) attempt 3, and (d) attempt 4
Table 3. Ra and Rmax depth values of pure Cu under three levels of downforce in 0.01M H₃PO₄+0.5 V

| Setpoint | Ra(nm)   | Rmax(nm) |
|----------|----------|----------|
| 0.4v     | 11.696   | 188.36   |
| 0.8v     | 9.978    | 152.27   |
| 1.2v     | 20.319   | 180.25   |

Figure 20. Changes in Ra of pure Cu under different downforce in 0.01M H₃PO₄ + 0.5 V

Figure 21. Changes in Rmax of pure Cu under different downforce in 0.01M H₃PO₄ + 0.5 V

3.4. Effects of a NECAM-Processed Probe

A scanning electron microscope was used to examine the surface morphology of an AFM probe after it was processed through NECAM under different environmental conditions, as shown in Fig. 4.

Fig. 22(a) shows that the unprocessed OTR-8 probe was intact and clean. After machining, a small amount of oxide scraped off the Cu surface and adhered to the probe, as shown in Fig. 22(b).

Figure 22. Probe morphology after machining in different environmental conditions: (a) Morphology of unprocessed OTR-8 probe (b) Morphology of probe following Cu machining in air, 0.01M H₃PO₄, and 0.01M H₃PO₄ + bias

4. Conclusions

This study adopted an ECAFM to conduct NECAM in a liquid environment. Pure Cu was used as the specimen, and Cu materials were subject to AFM machining under different environmental conditions. The results revealed that the Cu block effectively resisted corrosion when it was processed using an ECAFM in a liquid environment. When machining time was increased, increasing downforce in air did not significantly influence the Cu specimen. In 0.01M H₃PO₄, applying a small amount of downforce and bias voltage resulted in a significant machining outcome. In the presence of both 0.01M H₃PO₄ and bias voltage, a trace amount of CuO was found attached to the probe.

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