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Scanning Tunneling Microscopy of Copper Electrodeposited in the Presence of Benzotriazole

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SCANNING TUNNELING MICROSCOPY OF COPPER ELECTRODEPOSITED IN THE PRESENCE OF BENZOTRIAZOLE

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Applications of scanning tunneling microscopy (STM) to electrochemical metal deposition and oxidation have been reported by several researchers [1-4]. In the present work, the effects of benzotriazole (BTA) on the topography of Cu deposited on a Pt <111> single crystal surface under potential control was investigated with STM. The surfaces of the Cu deposits were continuously scanned with the tunneling probe during deposition. In the presence of BTA the initial monolayer of Cu was detected.

A Digital Instruments Inc. Nanoscope I STM with a 0.6 μm scanner was used. Horizontal positioning of the STM probe was under computer control. The data aquisition program produced a 320 by 200 point scan independent of area scanned. A grey scale image of $\frac{dz}{dx}$ is used to present the data where z is the probe distance from the surface and x is the distance in the probe raster direction.

Platinum tunneling probes were coated with polyvinylidene fluoride to reduce the electrochemically active area. The coating left a small area at the probe tip uncovered from which a background current of 0.2 nA at 100 mV vs Cu was measured in the electrolyte with a separation of tip and surface of greater than 1 μm. During STM operation, it is important to hold the probe potential in a region where no Faradaic reaction occurs on the probe. The probe potential was therefore restricted by the potentials of copper deposition and platinum oxidation. In this experiment, the STM was operated in a constant tunneling current mode (2 nA) with a probe bias of 100 mV vs the sample.

The electrochemical apparatus contained copper reference and counter electrodes in addition to the platinum working electrode. The reference and counter electrodes were contained in external cells connected to the working cell by capillary tubing. An electrolyte volume of 0.05 ml was retained on the Pt electrode with a polypropylene ring of 7mm inside diameter and 3mm height. The Pt <111> substrate was mechanically polished with 0.05 μm alumina, etched in warm aqua regia, and annealed at 1000 C for 12 hours. Copper was electrodeposited from an electrolyte of 10 mM $Cu(ClO_4)_2$ and 0.5 M $NaClO_4$ at a pH of 2 with and without 10 μM BTA. The Pt substrate was held at a potential of 100 mV vs Cu prior to Cu deposition.

The deposit from BTA-free electrolyte was initiated with a 30 sec pulse to -500 mV vs Cu with the tip removed from the surface. Following the 30 sec pulse the potential was stepped to -25 mV vs Cu at which time continuous scanning of the surface by the tunneling probe began. The deposit from BTA-free electrolyte had long range order exceeding the width of the probe scan, 0.6 μm (fig. 1). These deposits showed faceting with deposition observed at the edges. Although rapid growth is observed in some areas of the electrode little change occurs in others, this can be seen by comparing the top and bottom portions of figures 1a and 1b. Short period roughness resulting from new nucleation is shown in the bottom right corner of figure 1b. The deposit from BTA-containing electrolyte was initiated with a 0.5 sec pulse to -500 mV vs Cu. The tip was at tunneling distance from the surface during the initial pulse. Following the 0.5 sec pulse the potential was stepped to -20 mV vs Cu. Before Cu deposition the bare Pt surface showed a stepped appearance with 20 A ledges and atomically flat planes in between (fig 2a). Following the initial pulse, deposition on the Pt planes resulted in a wavy surface with a period of approximately 200 A and an amplitude of 5 A (fig 2b). This waviness is proposed to represent the island growth of the first monolayer of deposit. Following further deposition, the development of larger oblong nuclei of approximately 20 A height occurs. The deposit from the BTA-containing electrolyte did not show any faceting or long range order (fig. 2b,c) unlike the faceting shown for the BTA-free deposit (fig 1).

The propagation of edges and the long range order of the deposit from a BTA-free electrolyte indicates growth in preferred crystallographic directions. This preference is prevented by the action of BTA and random growth occurs. In the presence of BTA the Cu deposit develops from atomic height nuclei which coalesce into larger entities.

Acknowledgment:

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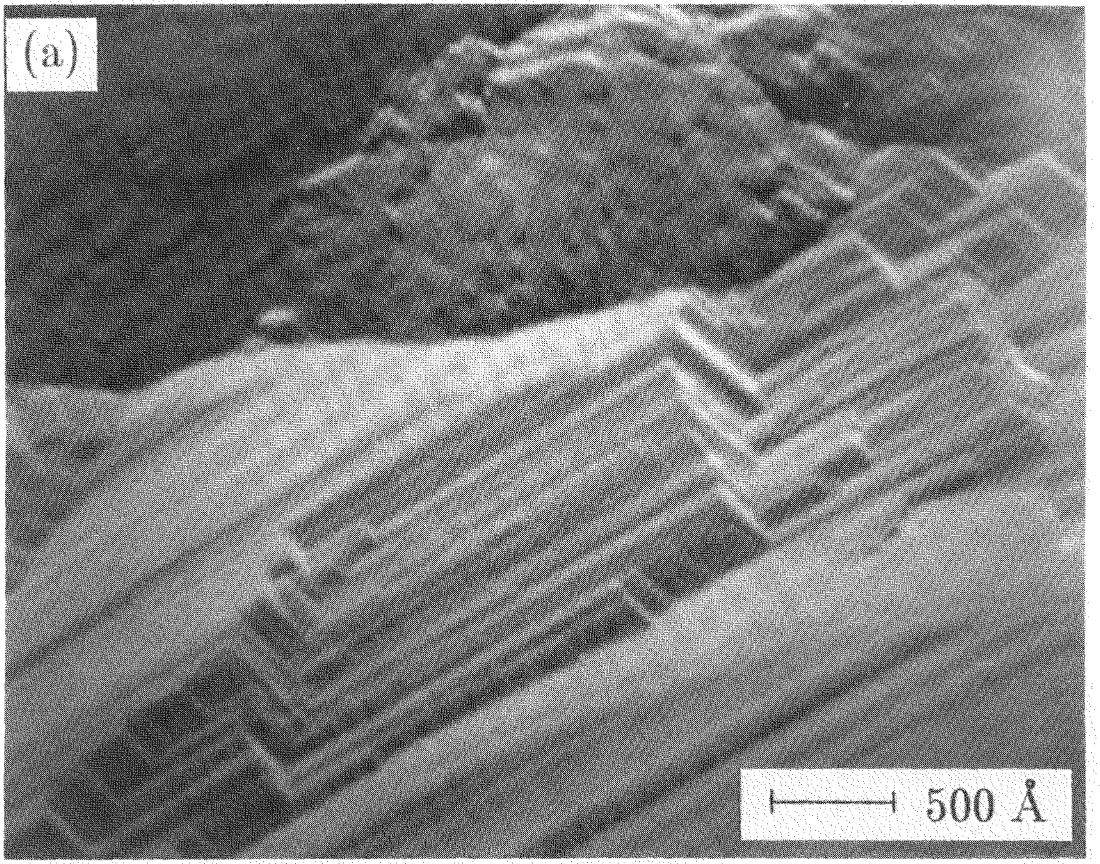
Figure 1.

Gray scale image of $\frac{dz}{dx}$ of electrochemically deposited Cu on Pt in the absence of BTA. 10 mM $Cu(ClO_4)_2$, 0.5 M $NaClO_4$, pH = 2. (a) initial image at -25 mV vs Cu following 30 sec pulse to -500 mV (XBB 880-11213), (b) after additional 60 sec of deposition at -25 mV vs Cu (XBB 880-11214). mV.

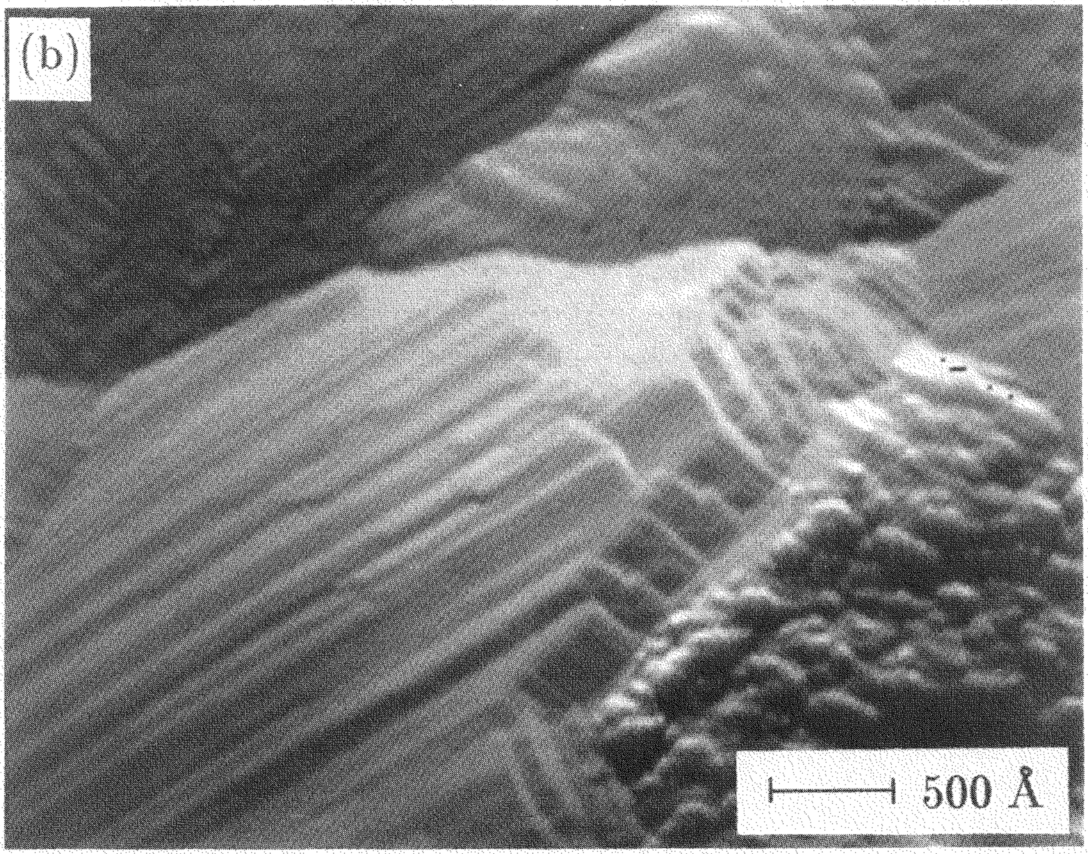
Figure 2.

Gray scale image of $\frac{dz}{dx}$ of electrochemically deposited Cu on Pt in the presence of BTA. 10 mM $Cu(ClO_4)_2$, 0.5 M $NaClO_4$, 10 μM BTA, pH = 2. (a) initial bare Pt surface (XBB 880-11210), (b) initial image at 20 mV vs Cu following 0.5 sec pulse to -500 mV (XBB 880-11211), (c) after additional 90 sec of deposition at -20 mV vs Cu (XBB 880-11212).



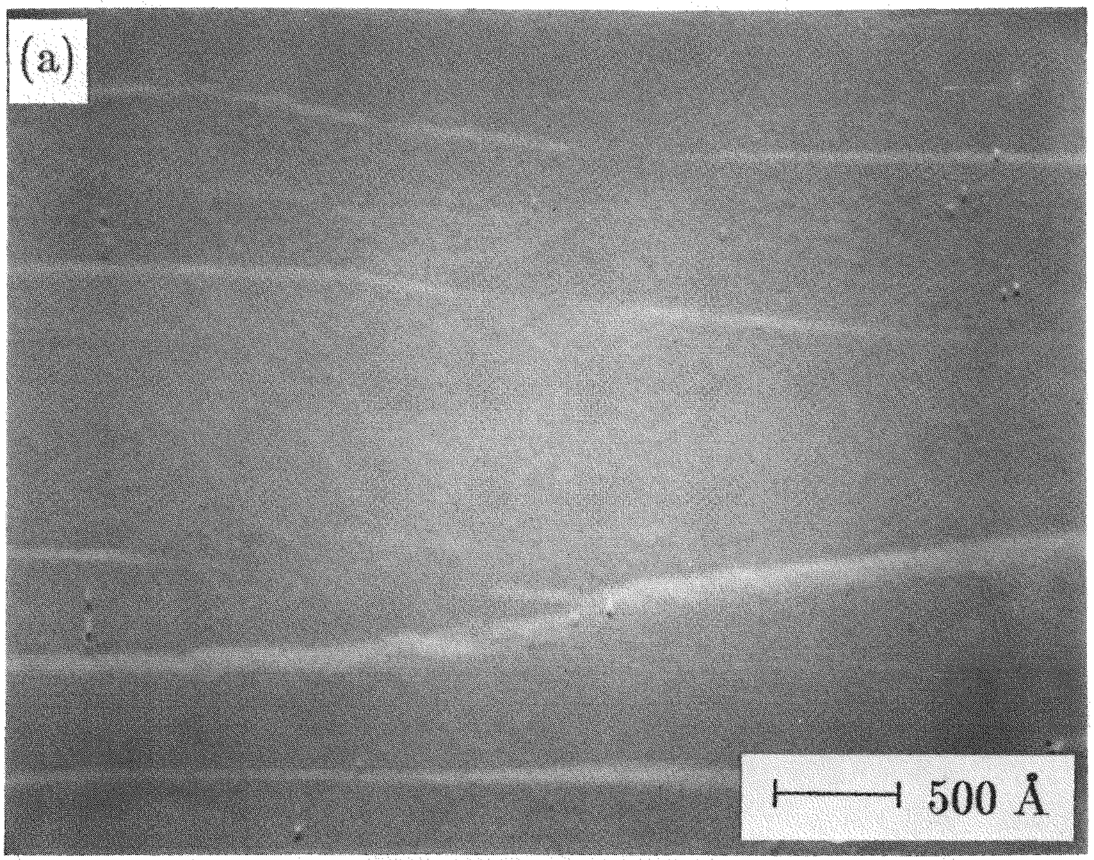
XBB 880-11213

Figure 1-a



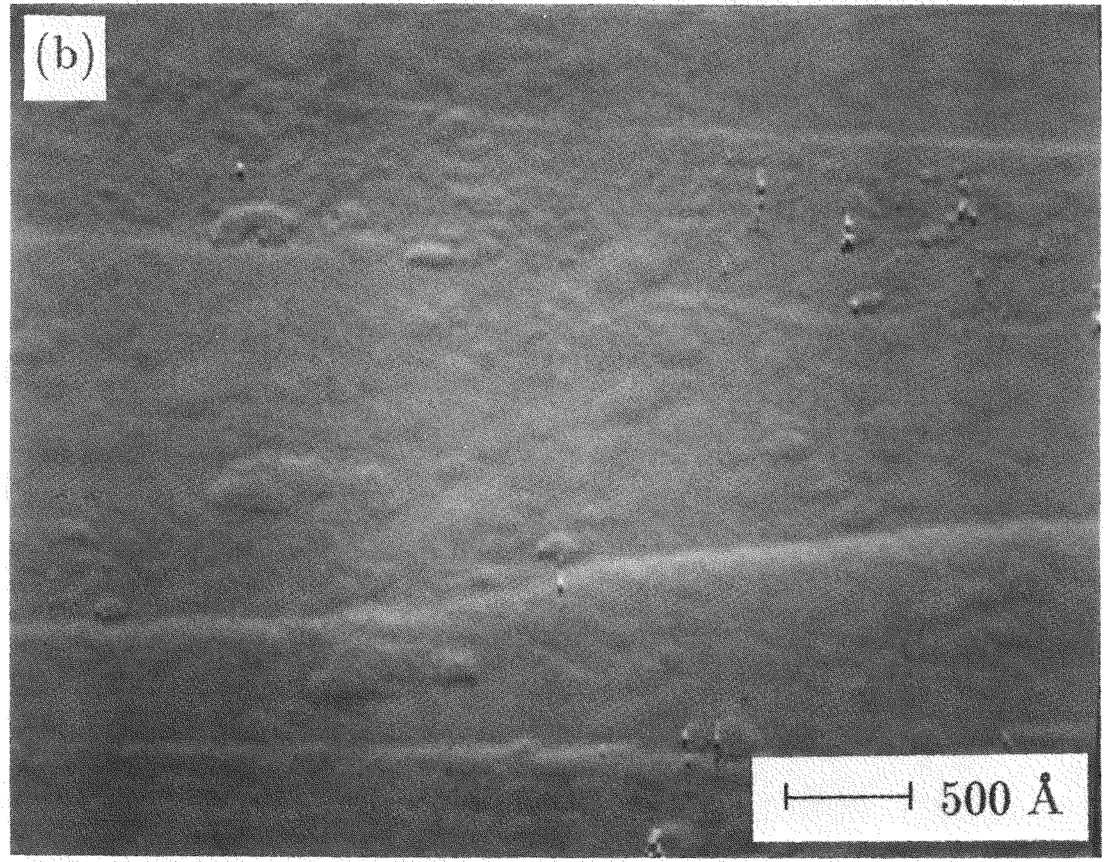
XBB 880-11214

Figure 1-b



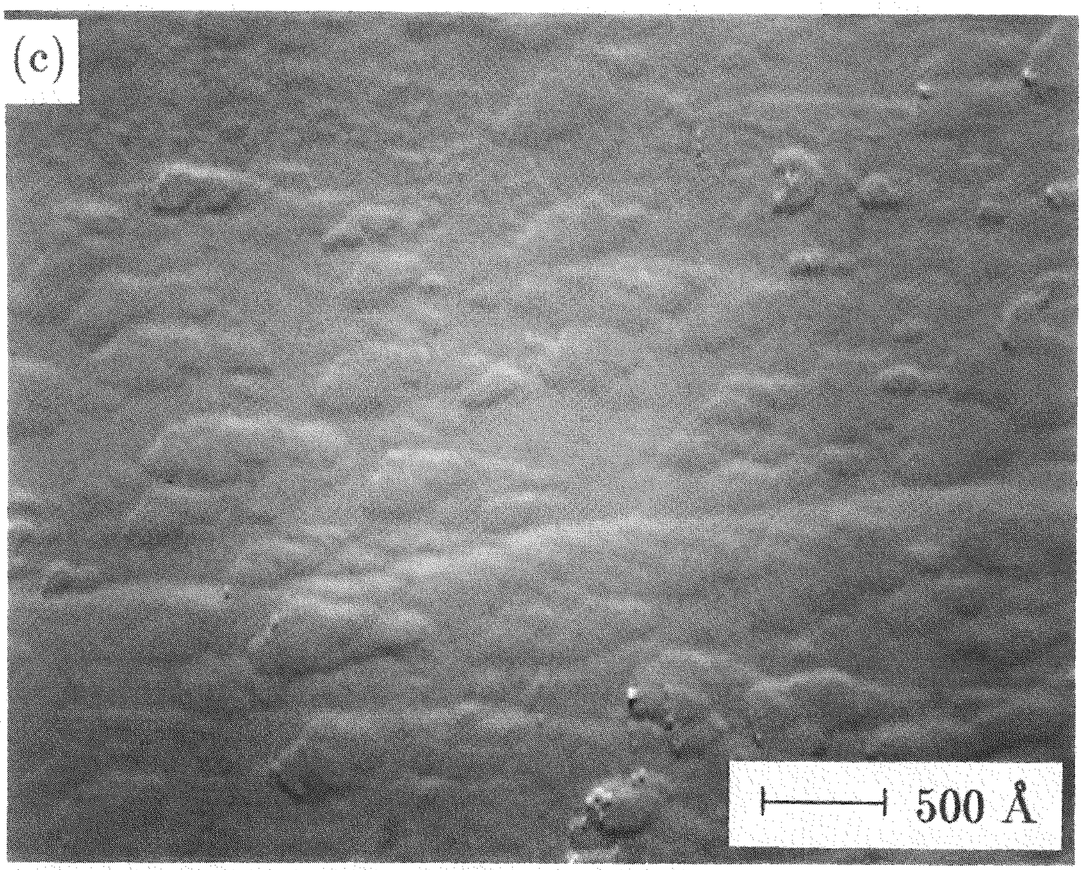
XBB 880-11210

Figure 2-a



XBB 880-11211

Figure 2-b



XBB 880-11212

Figure 2-c