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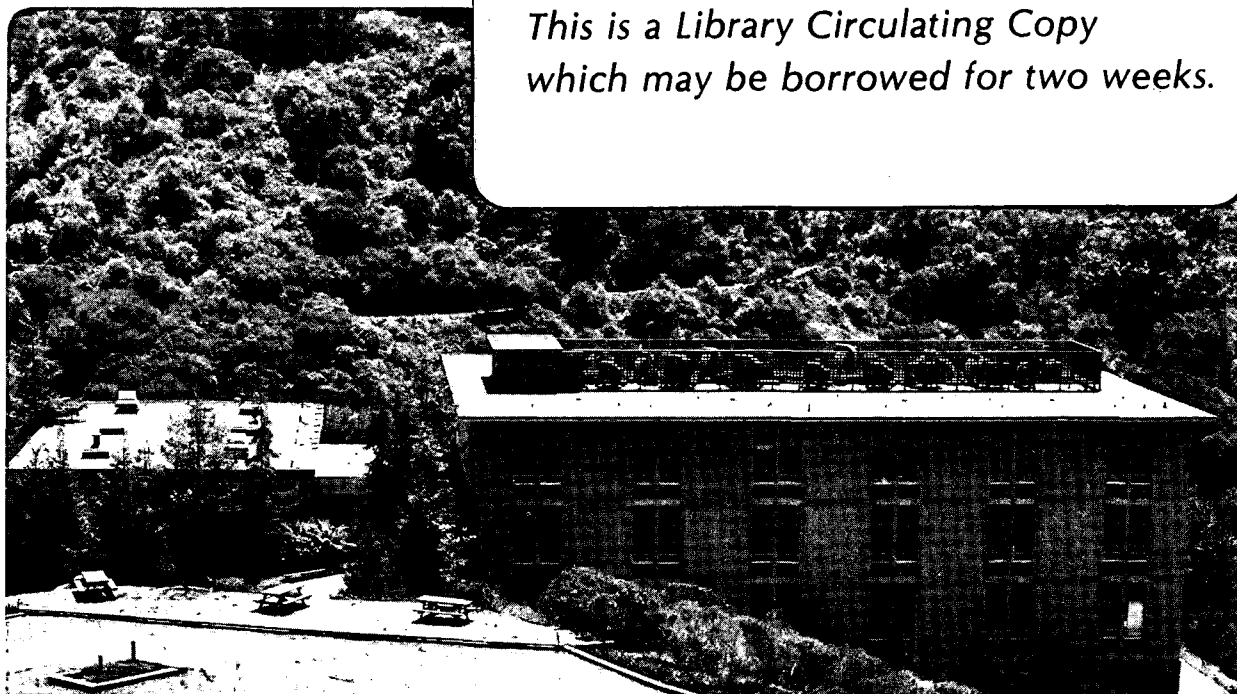
### STM Observations of Electrodeposited Copper under Potential Control and Open Circuit

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September 1988

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**STM observations of electrodeposited copper under potential control and open circuit**

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Applications of scanning tunneling microscopy (STM) to electrochemical metal deposition and oxidation have been reported by several researchers [1-7]. Open circuit conditions are encountered during transfer of electrochemical deposits for ex-situ measurements. In the present work, the topography of Cu deposit under potential control and at open circuit has been investigated by STM. Some preliminary results are reported here from a deposit of Cu on Pt from a 5 mM  $\text{Cu}(\text{ClO}_4)_2$  and 0.5 M  $\text{NaClO}_4$  solution of pH 2.

A Digital Instruments Inc. Nanoscope I STM with a 0.6  $\mu\text{m}$  scanner was used. Horizontal positioning of the STM probe was under computer control. The data acquisition program produced a 320 by 200 point scan independent of area scanned.

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. During STM operation, it was important to hold the probe potential in a region where no Faradaic reactions occurs between surface and probe. Thus the probe potential was restricted by the potentials of copper deposition and platinum oxidation. In this experiment, the STM was operated in a constant current mode with a sample to probe bias of -100 mV.

The electrochemical apparatus contained copper reference and counter electrodes in addition to the platinum working electrode. The reference and counter electrodes were contained in outside 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  $\langle 111 \rangle$  substrate was mechanically polished with 0.05  $\mu\text{m}$  alumina and etched in warm aqua regia.

Potentiostatic copper deposition was initiated by a potential step from +50 mV to -50 mV vs Cu. The current, measured under identical conditions with but without operating the STM, was initially 0.2  $\text{mA}/\text{cm}^2$  and decreased to 0.05  $\text{mA}/\text{cm}^2$  after 3 min. The rate of deposit growth, derived from the rate of vertical probe displacement, between 1 min and 1.5

min of deposition was approximately 1000 A/min. This rate of growth corresponds to 4 mA/cm<sup>2</sup> of 40 times the average current density of 0.1 mA/cm<sup>2</sup> indicating a highly non-uniform current distribution. Following 4 min of deposition, the solution was depleted of copper and deposit growth virtually ceased. The total thickness of the deposit under the probe was greater than 300 nm, as determined from the probe displacement upon dissolution of the deposit at the conclusion of the experiment. A uniform film of 70 nm thickness would form from deposition of all copper in solution in the volume of the cell.

No change of the surface was observed under potentiostatic control for 3 minutes after depletion of copper. The stable surface showed atomically smooth regions with single and multiatomic steps (fig. 1). Following 6 min of potentiostatic control, the cell was placed on open circuit: immediate dissolution of the surface occurred with an initial rate of 120 A/min slowing to 60 A/min after 2 min. The resulting surface is flatter with loss of its stepped appearance and development of atomic roughness (fig. 2). This observation illustrates the rapid change in microtopography that may occur during the transfer of specimens.

The present results show that current distribution for the initial stages of Cu deposition on Pt is nonuniform on the submicroscopic scale. The STM of electrodeposited copper showed steps of atomic height which are stable under potentiostatic control but disappear rapidly at open circuit.

#### **Acknowledgment:**

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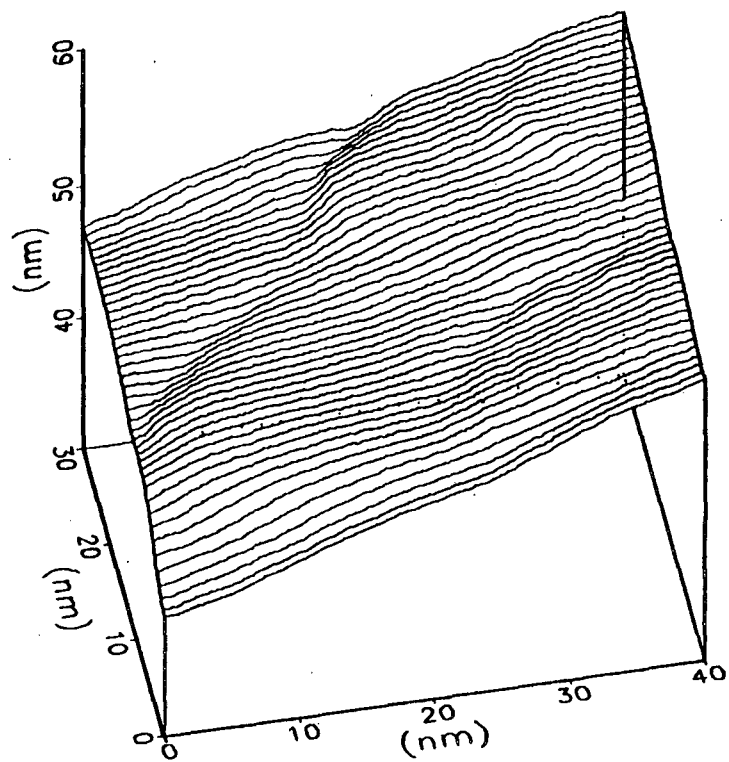


Fig. 1. Line Plot of electrochemically deposited Cu on Pt at -50 mV vs Cu, 5 min after deposit initiation, 10 mM  $\text{Cu}(\text{ClO}_4)_2$ , 0.5 M  $\text{NaClO}_4$ , pH = 2.



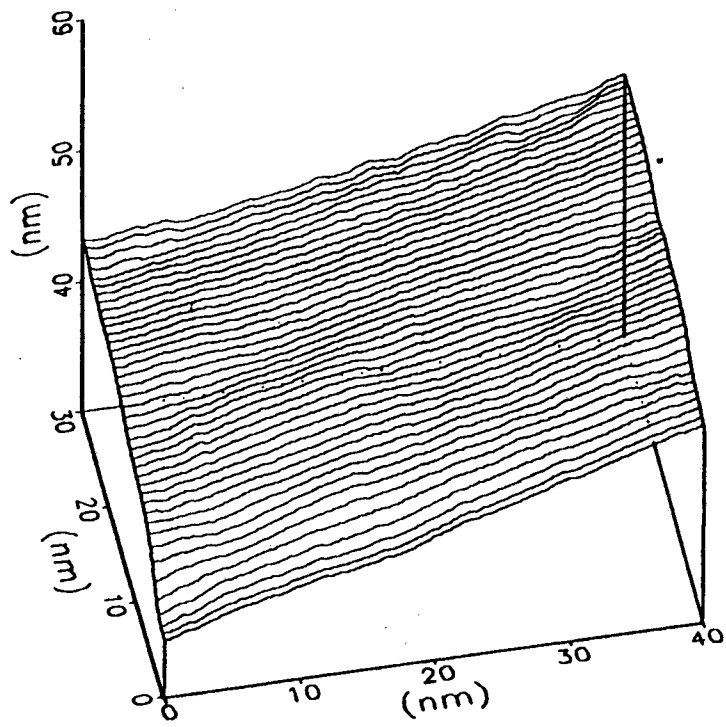


Fig. 2. Line Plot of electrochemically deposited Cu on Pt after 1 min at open circuit, 10 mM  $\text{Cu}(\text{ClO}_4)_2$ , 0.5 M  $\text{NaClO}_4$ , pH = 2.

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