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Nucleation of Copper Films on Platinum: Effect of Benzotriazole

Authors
Armstrong, M.J.
Muller, R.H.

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UNIVERSITY OF CALIFORNIA

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M.J. Armstrong and R.H. Muller

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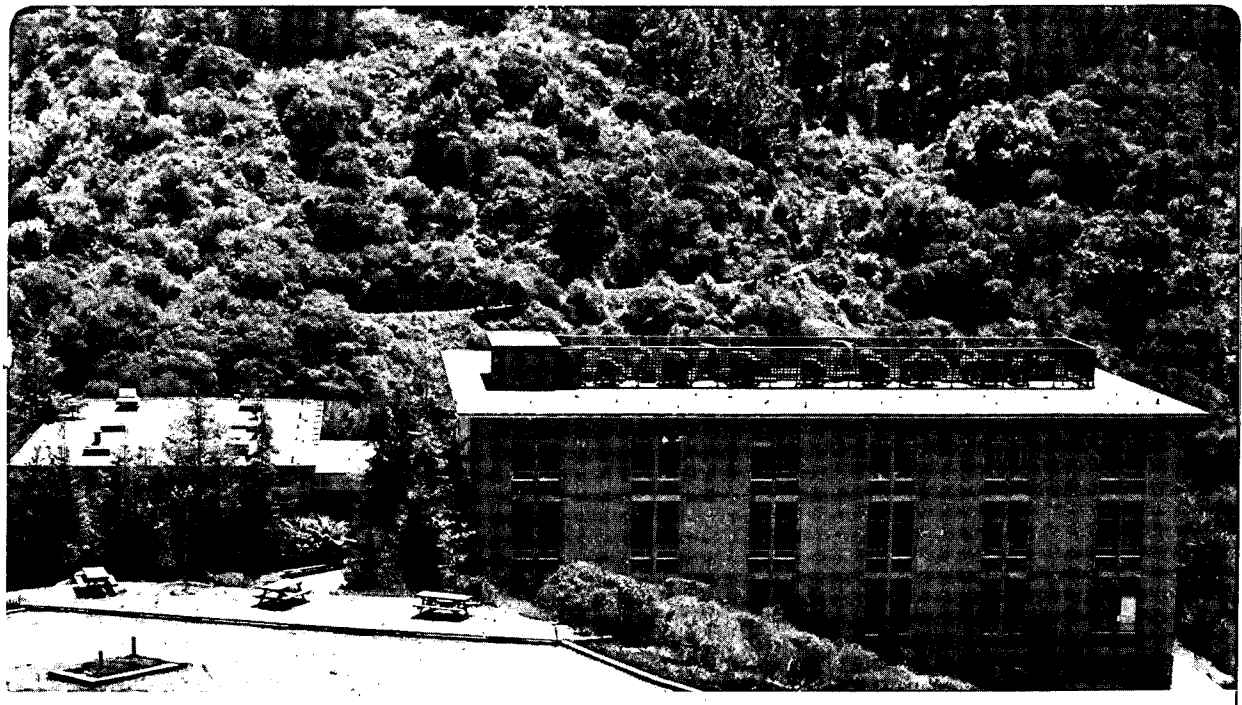

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DISCLAIMER

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M.J. Armstrong and R.H. Muller

Department of Chemical Engineering
University of California

and

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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NUCLEATION OF COPPER FILMS ON PLATINUM
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M. J. Armstrong* and R. H. Muller

Department of Chemical Engineering
University of California, Berkeley
and
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Background

The sub-micron topography of Cu deposits during the initial stages of deposition was studied with scanning tunneling microscopy (STM) to investigate the effect of benzotriazole (BTA). The brightness of a surface, characterized by a low intensity of scattered light, has been related to its topography.[1] Additives such as benzotriazole are used in plating baths to reduce the roughness. The average particle size in a deposit can be determined by dividing the deposition rate by the nucleation rate. In this study the number density of nuclei of Cu on Pt was derived from Fourier transforms of the STM data from 54 Å thick Cu films. The effects of BTA concentration and overpotential on the Cu number density of nuclei were determined.

Procedures

A Nanoscope I STM with a 0.6 μm scanner was used in this investigation.[2] The instrument was augmented with a PC-based data acquisition system for digitally recording STM images as 200 x 320 point maps of the probe height. Platinum wires, cut with scissors, were used for the tunneling probes. Scanning electron micrographs of the tunneling probes showed typically a 500 Å radius of curvature at the tip. Although very

* Current Address: IBM Corporation, Almaden Research Center, San Jose, CA, 95120-6099.

sharp tips could be made by this method, there was a frequent occurrence of multiple tunneling points. The probe potential was restricted by the potentials of Cu deposition and O_2 evolution in the Cu plating electrolyte. The background current on Pt probes in the Cu plating electrolyte was reduced from greater than 20 nA to less than 1 nA (at a probe potential of 100 mV vs Cu) by applying a coating of polyvinylidene fluoride. All STM measurements reported below were obtained with the constant current method (2 to 5 nA).

The electrochemical cell contained four electrodes: deposit substrate, counter electrode, reference electrode, and tunneling probe. The tunneling probe was held at constant potential (30 mV) relative to the substrate by the Nanoscope I controller. The probe current was maintained by the probe surface separation. The potential of the substrate relative to the reference electrode or the current between the substrate and the counter electrode was controlled by a PAR 173 potentiostat. Electrical isolation of the potentiostat is necessary to prevent current loops between the potentiostat, STM controller, and ground. The potentiostat was connected to the 120 V_{AC} line with an isolation transformer and connected to ground through a 100 μF capacitor. The electrochemical cell consisted of a Pt (110) substrate on which approximately 0.1 ml of electrolyte was held by a 6 mm diameter Pt ring (made from 10 mil wire) located 1 mm from the substrate surface. The Pt ring also served as the counter electrode. A Cu wire was used as a reference electrode. The composition of the electrolyte was 0.5 M $CuSO_4$ and 0.5 M H_2SO_4 with 0, 50, 100, or 200 μM BTA. The substrate was mechanically polished with 0.05 μm alumina and annealed in a natural gas flame. Prior to each deposition the substrate was cleaned by passing an anodic current of 1.6 A/cm^2 for approximately 4 s followed by a change of electrolyte. The copper deposit was made with a galvanostatic pulse. Following the pulse a constant current was applied to prevent deposit dissolution resulting from oxygen reduction. The level of the oxygen reduction current was determined from measurements on the Pt substrate at +2 mV vs Cu. The tunneling probe was withdrawn from solution during the cathodic pulse to prevent shielding of the substrate by the tip. Profiles of the nucleated deposit and of the substrate were taken. The deposit was removed by electrochemical dissolution in order to determine the profile of the substrate. The number density of nuclei was estimated from a one dimensional fast Fourier transform (FFT) of the probe height with respect to the scan direction. The amplitudes from the FFT of the data were averaged over the 320 raster lines of the STM scan. This analysis was based on the assumption that the ratio of height to width of nuclei was constant. If the nuclei on the surface are touching and not overlapping, the characteristic frequency, f_s, of the surface is equal to the inverse of the width of the nuclei such that the product of the

amplitude and frequency is constant irrespective of number density of nuclei. The characteristic frequency was experimentally determined as the frequency at the peak value of the product of amplitude and frequency from a FFT of the surface. The number density of nuclei was estimated as $(f_s)^2$.

Results

Figure 1 is the image of a typical substrate surface following dissolution of the copper deposit. The surface consisted of 100 Å wide terraces separated by 10 to 30 Å high steps. Figure 2 is the image of a Cu deposit formed in 100 μM BTA with a 200 ms 100 mA/cm^2 pulse. The underlying Pt substrate appears to be completely covered with Cu particles with radii less than 500 Å. Figure 3 shows the frequency dependence of the product of amplitude and frequency from Fourier transforms of the STM data of figures 1 and 2. As based on the Fourier analysis, the surface imaged in figure 2 has a spatial period of 320 Å corresponding to $9.8x10^{10}$ nuclei/cm^2.

Conclusions

The number density of nuclei shows an upward trend with increasing overpotential, with no significant difference between electrolytes containing 0, 50, 100, and 200 μM BTA (figure 4). It appears therefore that the number density of nuclei is only dependent on the overpotential.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

References

1) O. Kardos and D. G. Foulke, in **Advances in Electrochemistry and Electrochemical Engineering**, Vol 2, C. W. Tobias Ed., Interscience, New York, 1962.

2) Digital Instruments Inc., Goleta, California, 93117, USA.

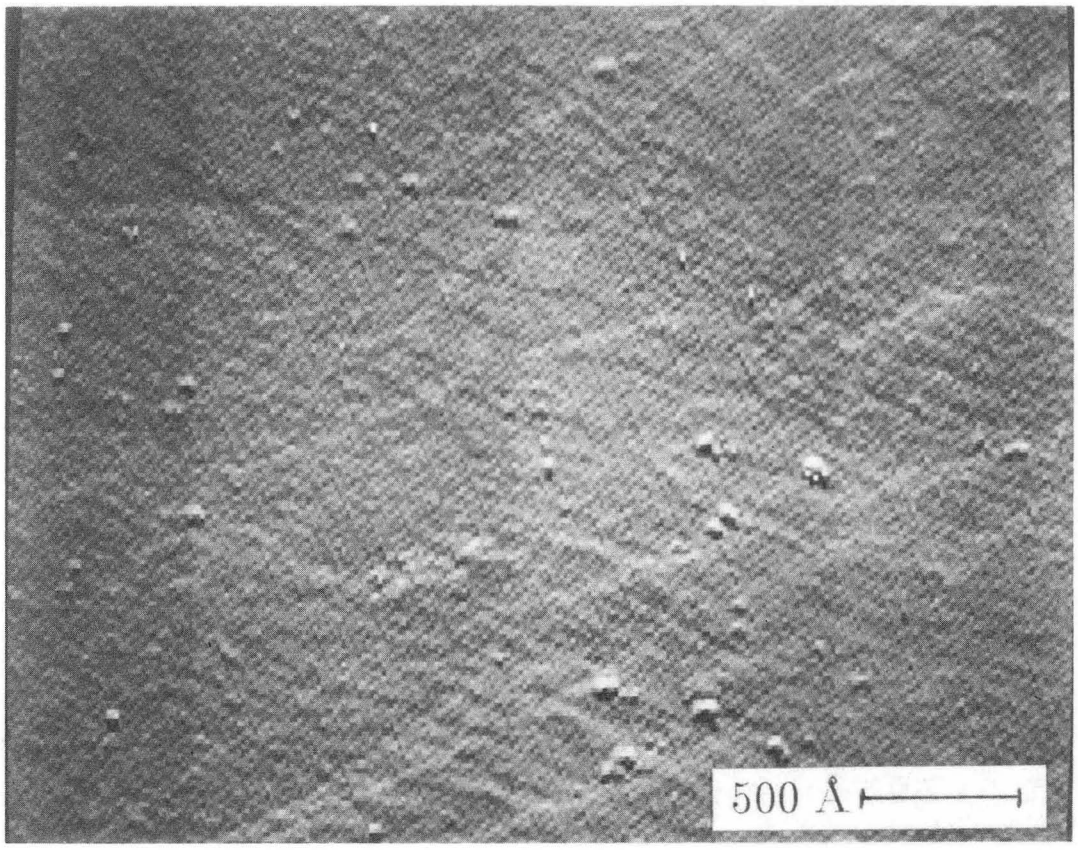

Figure 1. STM image of a flame annealed Pt substrate; displayed with a derivative coded grey scale. The surface consisted of 100 Å wide terraces separated by 10 to 30 Å high steps. There are also a small number of protrusions on the surface. (XBB 901-555)

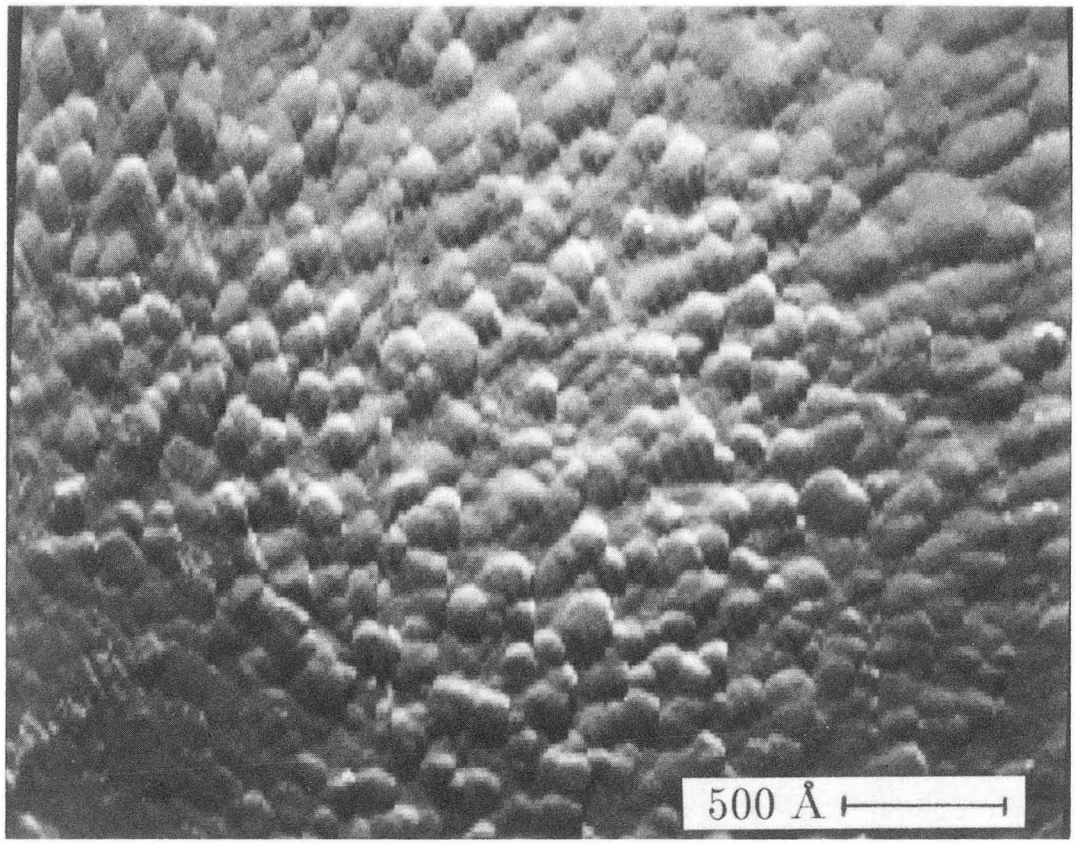

Figure 2. STM image of a 20 mC/cm^2 Cu deposit on a Pt substrate (shown in figure 1.); displayed with a derivative coded grey scale. The deposit was formed by a 100 mA/cm^2 pulse in 0.5 M $CuSO_4$, 0.5 M H_2SO_4, with 100 μM BTA. FFT of the deposit contour indicates the nuclei have a periodicity of 320 Å (9.8x10^{10} nuclei/cm^2).
(XBB 901-554)

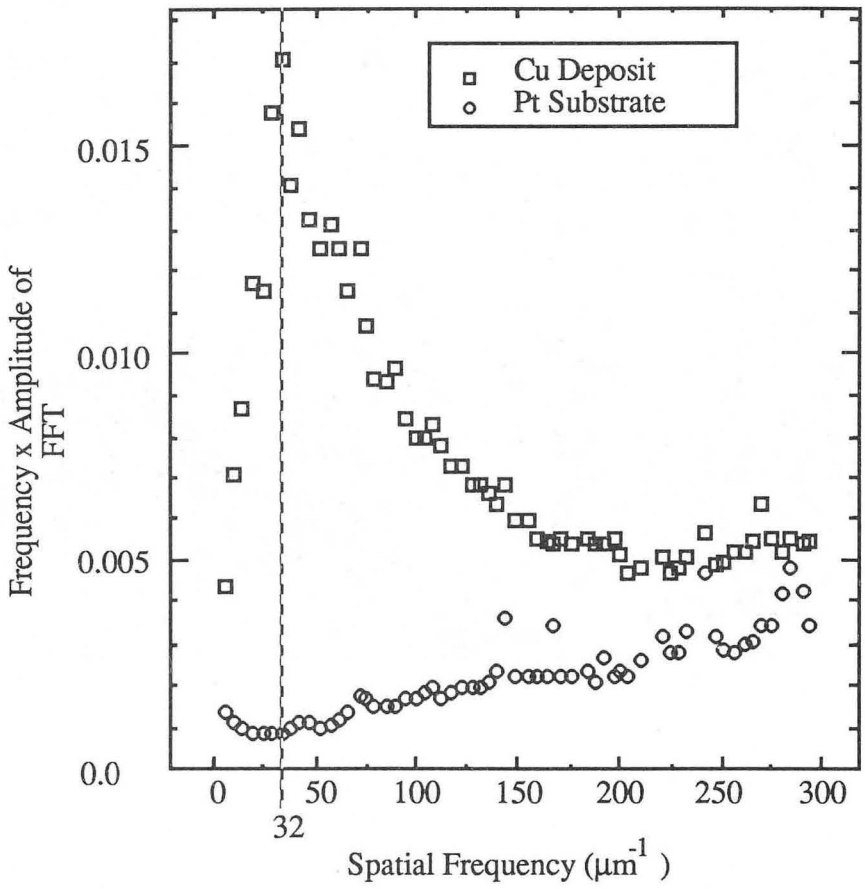

Figure 3. FFT of the probe height with respect to the distance in the scan direction of a (◘) 20 mC/cm^2 Cu deposit and the (o) underlying Pt substrate. The Cu deposit was formed by a 100 mA/cm^2 pulse in 0.5 M $CuSO_4$, 0.5 M H_2SO_4, with 100 μM BTA. FFT of the deposit contour indicates the nuclei have a periodicity of 320 Å (9.8×10^{10} nuclei/cm^2). (XBL 902-572)

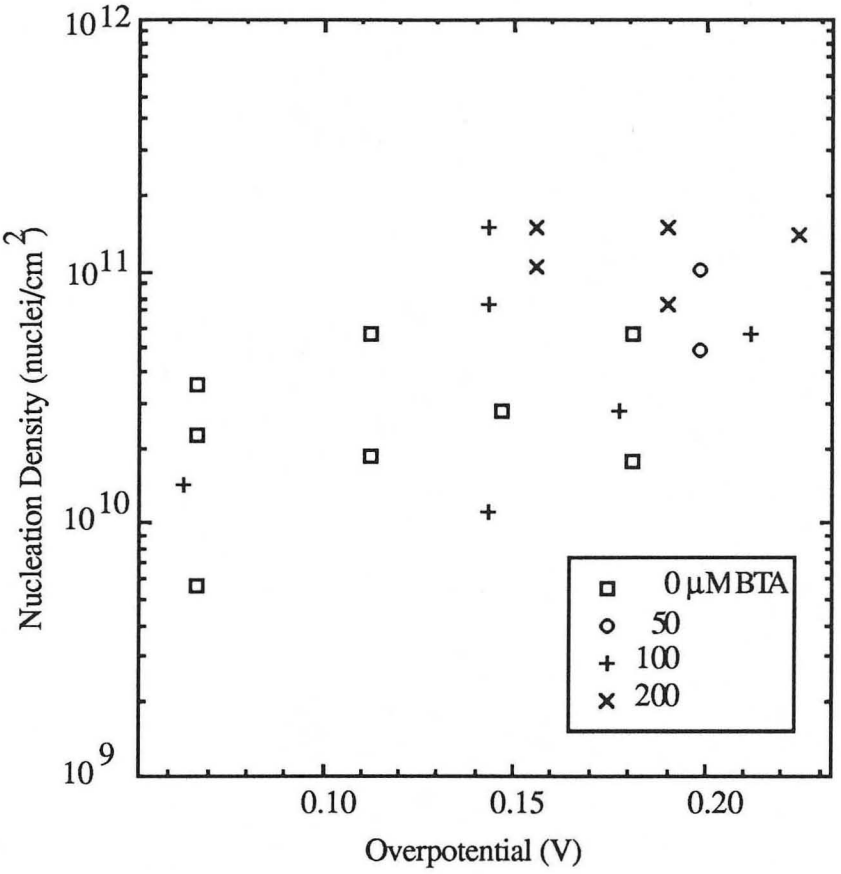

Figure 4. Effect of overpotential and BTA concentration on the number densities of nuclei of 20 mC/cm^2 Cu deposits on Pt. The number densities of nuclei were derived from FFT of the deposits. The Cu deposits were formed from 0.5 M CuSO4, 0.5 M H_2SO_4, with (▣) 0, (o) 50, (+) 100, and (x) 200 μM BTA. (XBL 902-607)

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720