Pattern-Recognition Studies of Copper Electrodeposition on Cu(100) in the Presence of Additives

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Square pyramidal mounds that have been observed in epitaxial growth of the Cu(100) surface during both electrodeposition[1,2] and molecular beam epitaxy.[3] There is theoretical evidence that (100) surfaces are kinetically unstable to the growth of square-pyramidal mounds under some growth conditions.[4-6] The appearance of mounds on 100 surfaces has been attributed to surface diffusion processes. The mound instability may appear if there exist energetic barriers to diffusion across steps, short-range interactions between adatoms and steps, a step-edge diffusion process or limited-mobility diffusion generally. Depending on the mechanism of surface diffusion and attachment of adatoms or adions, the slope of the mounds may approach a steady-state or 'selected' value. In this study, we apply pattern recognition procedures to identify and characterize the shapes of surface features that arise during electrodeposition of copper on Cu(100) both with and without organic additives that may adsorb and modify surface processes.[7]

An atomic-force microscope (AFM) image provides an array of surface heights h_{ij}. Pattern-recognition analysis of the image proceeds through two steps. [11] In the first step, features in the AFM image are located by convolution (c_{nm}) of a template a_{ij} and the surface height h_{nm}. Local maxima in c_{nm} indicate the presence of features similar to the template, and the magnitude of a local maximum is a measure of the degree of similarity. The second step in the procedure is to optimize the match between template and surface feature at points where c_{nm} is large. The optimized template can then be used to calculate geometric properties, such as local slopes, of the features.

Cu(100) surfaces were imaged by AFM. The additive-free plating solution was *0.2 M* $CuSO_4$*/1.0 M* H_2SO_4*1.0/mM HCl,* Two additional solutions were produced by adding *100 μM* benzotriazole (BTA) or *100 μM* 3-mercapto-1-propanesulfonic acid (MPSA) to the additive-free solution. The applied cell current was 10 *mA*, corresponding to about 30 mA/cm^2. To prevent the interfacial concentration of copper sulfate falling to less than 70 percent of the bulk concentration, a square-wave pulse-current program was imposed.

Figure 1 shows a surface after a deposition time of 50 seconds in additive-free solution. The main features are square pyramidal mounds. Figure 2 shows a deposit formed in MPSA solution for the same deposition time.

The correlations of square-pyramid, cone and hemispheroidal templates with deposits formed in Chloride, BTA and MPSA solution are shown in Table 1. In additive-free solution, the square pyramid template provides the best fit. In BTA solution, the main features are rounded nodules, and the hemispheroidal template provides the best fit. In MPSA solution, none of the three templates provided a satisfactory fit to the surface.

Figure 3 is a plot of mound-slope versus deposition time for the pyramids formed in additive-free solution. The slope increases monotonically, with no tendency to a steady or selected value. Figure 4 is a plot of the aspect ratio of height to base radius for a hemispheroidal template fitted to the nodules formed in BTA solution. The aspect ratio increases linearly with time.

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Solution / Run	Pyramid	Hemisphere	Cone
Cl^- / 1	0.94	0.77	0.81
Cl^- / 2	0.91	0.81	0.82
Cl^- / 3	0.94	0.78	0.80
Cl^- / Avg	0.93	0.79	0.81
BTA /1	0.78	0.94	0.79
BTA / 2	0.79	0.92	0.80
BTA / 3	0.81	0.93	0.82
BTA / Avg	0.79	0.92	0.80
MPSA / 1	0.87	0.87	0.88
MPSA / 2	0.84	0.86	0.85
MPSA / 3	0.83	0.85	0.84
MPSA / Avg	0.85	0.86	0.86

Table 1: Template Correlation Coefficients

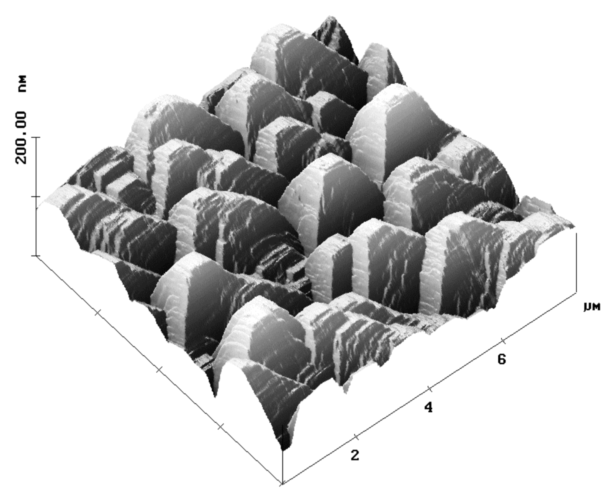

Figure 1. Cu(100) with pyramidal mounds formed in chloride solution without organic additives.

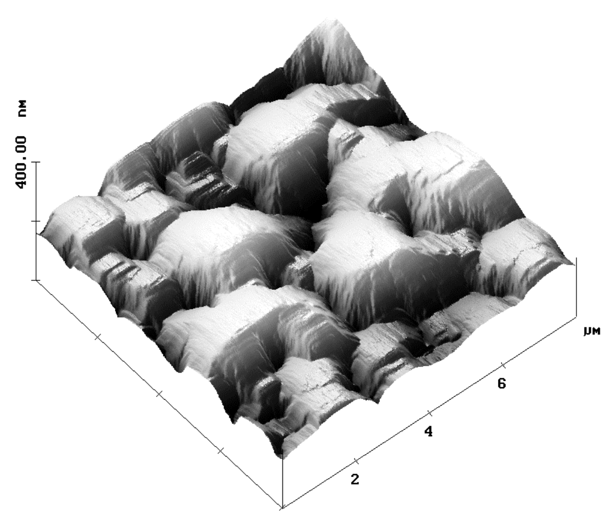

Figure 2. Surface of deposit on Cu(100) in MPSA solution.

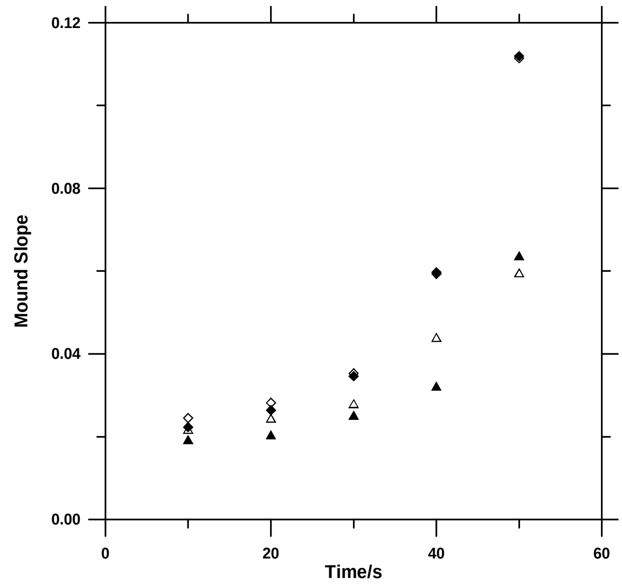

Figure 3. Mound slope versus deposition time for pyramids formed in chloride solution without organic additives.

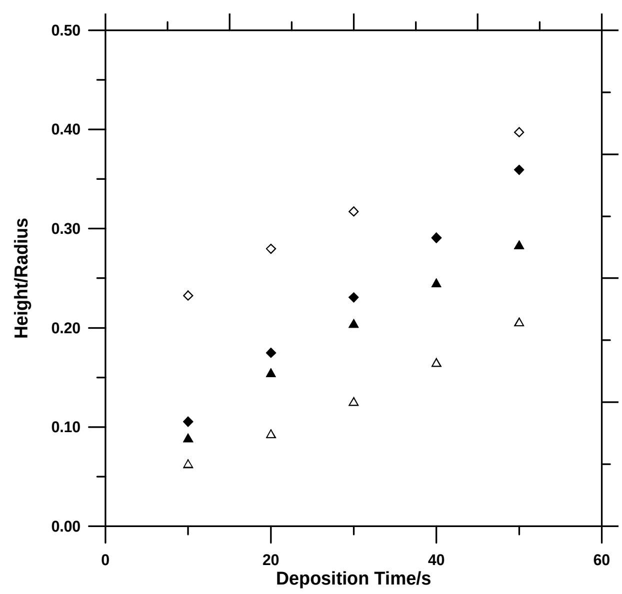

Figure 4. Ratio of height to base width versus deposition time for hemispheroidal growth centers formed in BTA solution