Surface Roughness Evolution for Cu Electrodeposition on Microelectrodes

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We have used atomic force microscopy (AFM) to measure the surface roughness of Cu films electrodeposited on photolithographically patterned microelectrodes. The data is consistent with anomalous scaling, where both the local and large-scale roughness have power law dependence on the film thickness. Our results point to the role of diffusion control in determining the scaling behavior. Although the current distribution was nonuniform, and both the film thickness and roughness were greater near the edge than at the center, the scaling exponents were the same wherever measured. Data from both the center and near the edge lie on a single line when saturation roughness $w_{sat}$ is plotted against correlation length $l_c$.

As a relatively inexpensive and fast fabrication technique, electrodeposition is playing a growing role in the production of microelectronic devices. In such applications it is often necessary to make very small structures by depositing a metal such as Cu into features produced by patterning a resist layer. This deposition can involve extremely nonuniform current distributions, which could be expected to affect the properties of the electrodeposited metal. In this paper we address the question of how patterning affects the surface roughness of Cu films electrodeposited on microelectrodes under diffusion control, focusing on how the different film growth rates across the electrode affect the roughness evolution. We have combined atomic force microscope (AFM) measurements with scaling analysis of the data. To our knowledge this is the first time that the roughness of electrodeposited films on microelectrodes has been studied quantitatively and systematically.

Surface roughening is a widespread phenomenon that occurs when material is added to or removed from a surface out of equilibrium. It has been studied for electrodeposition, electroless deposition, and many systems besides. Very often, surface roughening has been found to generate statistically self-affine surfaces that may usefully be described in terms of the surface width $w$, defined as

$$w(l) = \sqrt{\langle (h - \langle h \rangle)^2 \rangle}$$

where $h$ is the surface height and $l$ is the size of the region over which $w$ is measured.

For a growing film, $w$ is expected to change with the amount of material deposited, a situation referred to as kinetic roughening. In numerous models and some experimental systems kinetic roughening is well-described by so-called normal dynamic scaling, whereby $w(l)$ saturates for small $l$, and is proportional to $l^\beta$ for large $l$, where $l$ is the thickness and $\beta$ is a scaling exponent. Another group of models predicts a different kind of scaling, referred to as anomalous dynamic scaling, whereby $w(l)$ shows a power law dependence on $l$ even for small $l$. Anomalous scaling may be represented by the following expression

$$w(l,t) = l^{\beta_w}f(t/l^\alpha)$$

where the function $f(x)$ is constant for $x \gg 1$ and varies as $x^\delta$ for $x \ll 1$; $H$ is the Hurst exponent, and $\gamma (= H/\beta)$ is the dynamic exponent. If $\beta_w = 0$, the scaling is normal rather than anomalous.

For a given value of $l$, the crossover between these two scaling regimes occurs at $l = l_c \propto t^{1/\gamma}$, where $l_c$ is known as the correlation length. Hence we have

$$w(l,t) \propto \begin{cases} l^{\beta_w} & \text{for } l \ll l_c \\ l^\beta & \text{for } l \gg l_c \end{cases}$$

For a given $t$, the roughness increases as $t^\alpha$ and then saturates at a value $w_{sat}$, which is proportional to $t^{\gamma}$: $\alpha$ is known as the roughness exponent and, from Eq. 3, must obey the following equation

$$\alpha = H(1 + \beta_w/\beta)$$

Experimental

The substrates for these experiments were Au (25 nm)/Ti (5 nm)/glass, prepared by sputtering. Positive photoresist and UV photolithography were used to pattern individual microelectrodes (circular resist-free areas of 30 μm radius). A schematic cross section of a microelectrode is shown in Fig. 1. The resist thickness was approximately 1 μm.

Electrodeposition was performed potentiostatically in a three-electrode cell, without mechanical agitation. A saturated calomel (SCE) reference electrode was used and the electrolyte composition was 5 mM CuSO$_4$/0.5 M H$_2$SO$_4$. The potential was stepped from zero to $-550$ mV (vs. SCE) for the deposition time (between 60 and 1440 s) and current transients were recorded. The current transients and cyclic voltammetry experiments were consistent with the current being diffusion-limited at this deposition potential. After deposition, the electrodes were rinsed in ultrapure water, dried with N$_2$ gas, and imaged by AFM (Digital Instruments DI 3000) in contact mode, with silicon probes. Scans were taken with a resolution of either 256 × 256 or 512 × 512 pixels.

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Figure 1. Schematic cross section of a microelectrode. The gold substrate (working electrode) is masked by photoresist, apart from the patterned area. The arrows represent the flux of ions to the electrode: the diffusion limited current is greater at the edge than at the center.
Results and Discussion

Figure 2 shows $w(l)$ data calculated from a typical image. Log $w$ increases linearly with log $l$ for small $l$, and saturates for large $l$, consistent with Eq. 3. In order to determine $H$ (the gradient of the plot for small $l$), $w_{\text{sat}}$ (the value of $w$ for large $l$), and $l_e$ (the crossover between the two regimes), the following function was used to fit the data:

$$w(l) = w_{\text{sat}}[1 - \exp(-l/l_e)]^{1/2}$$

Clearly, Eq. 5 gives a good fit to the data, and fitting a single function is much less arbitrary than fitting separate straight lines to the linear parts of the curve, as was done in previous scaling studies of electrodeposited films. Each sample was imaged several times, and average values of $H$, $w_{\text{sat}}$, and $l_e$ were calculated for the center and edge regions separately. For our microelectrodes of radius 30 $\mu$m, we defined the center region as up to 5 $\mu$m from the center, while the edge region is between 15 and 25 $\mu$m from the center. Within error, $H$ was found to be constant for all deposition times and regions, taking the value $H = 0.84 \pm 0.02$.

Figure 3 shows $w_{\text{sat}}$ for the center and edge regions as a function of the total charge $Q$ passed through the electrode. $Q$ was calculated by integrating the current transients with respect to time, and was proportional to the total amount of material deposited. From the figure it is clear that for a given value of $Q$, $w_{\text{sat}}$ was considerably higher near the edge of the electrode, where growth was faster due to enhanced diffusion (the so-called edge effect—see Fig. 1), than near the center. From Fig. 3 it is also clear that log $w_{\text{sat}}$ increased linearly with log $Q$ in both regions. This means that in both regions $w_{\text{sat}}$ was proportional to $Q^B$, where $B$ may be calculated from Fig. 3. The exact relationship between $Q$ and the thickness $t$ at either the center or edge of the film is unknown. However, if we assume that $t(r)$ (where $r$ is the distance from the center of the electrode) is proportional to $Q$, then $w_{\text{sat}}$ is proportional to $t^B$ at both center and edge, and from Eq. 3, $B = \beta + \beta_{\text{loc}}$. Since, within error, the best fit straight lines to the edge and center data in Fig. 3 are parallel, we can conclude that $\beta + \beta_{\text{loc}}$ is the same at the center of the microelectrode and near its edge, and equal to 0.81 $\pm$ 0.06.

$^b$ The difference between $H$ calculated from $w(l)$ and $H$ calculated from the correlation function $G(l) = \sqrt{(\Delta x^2 + (l - \Delta x)^2)}$ is, however, greater than the quoted experimental error, which suggests extreme caution when comparing experimental values of $H$ with those predicted by simple theoretical models.

Figure 4 shows $w_{\text{sat}}$ as a function of $l_e$. Note that the same straight line fits both regions’ data, which means that $w_{\text{sat}}$ is given by $w_{\text{sat}} = k l_e^\alpha$ with the same constant of proportionality $k$, and the same scaling exponent $\alpha = 1.9 \pm 0.2$ for both center and edge regions. Since $w_{\text{sat}}$ measures the long-range roughness, and $l_e$ is a measure of the maximum lateral feature size, this shows that even though for a given charge $Q$ passed through the microelectrode, the edge region is always rougher than the center, the roughness at edge and center develop the same way (within error), in the sense that a given long-range roughness is associated with a particular lateral feature size.

In order to understand the rate at which the roughness evolves at edge and center, we need to combine information from Fig. 4 with other data. Since $H$ and $\alpha$ are the same at the center and near the edge of the microelectrode, Eq. 4 implies that $\beta_{\text{loc}}/\beta$ is also the same for both areas. Combining the value of $\beta_{\text{loc}}/\beta = 1.3 \pm 0.2$ obtained from Fig. 4 with the value of $\beta + \beta_{\text{loc}}$ obtained from Fig. 3 gives $\beta = 0.36 \pm 0.05$ and $\beta_{\text{loc}} = 0.45 \pm 0.05$. Because the value of $\beta_{\text{loc}}$ is different from zero, we can conclude that the scaling is anomalous.

Figure 5 shows $w_{\text{sat}}$ as a function of $l_e$ (correlation length) for the center and edge regions of the microelectrode. The straight line is a fit to the data and its gradient gives $\alpha = 1.9 \pm 0.2$. 
ties in the two regions are different. Therefore regions of the microelectrode, even though the actual current density should be diffusion-limited in both the edge and center. Furthermore, at the deposition potential chosen for the present study, the same. Table I shows that, within error, this is indeed the case. We used similar substrates, we expect electrolyte, although with a lower Cu concentration, and both studies diffused-limited value. Since the present study used a similar ele-

trolyte concentration or current density, while depended on our earlier assumption that depend on the electrolyte concentration or current density, and appeared to depend only on how close the current density was to its diffusion limited value. Table I shows that this, to the value determined in the previous study when the current density was close to its diffusion limited value.

Table I. Values of the three independent scaling exponents $H$, $\beta$, and $\beta_{\text{loc}}$ measured for the microelectrodes (this work) and for large-area planar electrodes when the current was 90% of the limiting current.$^a$

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Substrate</th>
<th>$H$</th>
<th>$\beta$</th>
<th>$\beta_{\text{loc}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005 M CuSO$_4$</td>
<td>Micro-electrode</td>
<td>0.84±0.02</td>
<td>0.36±0.05</td>
<td>0.45±0.05</td>
</tr>
<tr>
<td>0.5 M H$_2$SO$_4$</td>
<td>Micro-electrode</td>
<td>0.84±0.02</td>
<td>0.36±0.05</td>
<td>0.45±0.05</td>
</tr>
<tr>
<td>0.3 M CuSO$_4$</td>
<td>Planar electrode</td>
<td>0.75±0.05</td>
<td>0.42±0.05</td>
<td>0.40±0.03</td>
</tr>
</tbody>
</table>

It is important to note how useful plots of $w_{\text{sat}}$ against $t'$ like Fig. 4 can be, since they appear not to have been exploited in previous studies. They have the great advantage of providing information about roughness evolution that does not require knowledge of the film thickness. For example, our conclusion that $\beta_{\text{loc}}/\beta = 1.3 \pm 0.2$ (and consequently that the scaling is anomalous) does not depend on our earlier assumption that $t(r)$ is proportional to $Q$. The scaling exponents from this study may be compared with those found in an earlier study of Cu electrodeposition from organic additive-free acid sulphate electrolytes onto conventional large-area planar electrodes.$^4$ This earlier study found that $H$ and $\beta$ did not depend on the electrolyte concentration or current density, while $\beta_{\text{loc}}$ appeared to depend only on how close the current density was to its diffusion-limited value. Since the present study used a similar electrolyte, although with a lower Cu concentration, and both studies used similar substrates, we expect $H$ and $\beta$ for the two studies to be the same. Table I shows that, within error, this is indeed the case. Furthermore, at the deposition potential chosen for the present study, deposition should be diffusion-limited in both the edge and center regions of the microelectrode, even though the actual current densities in the two regions are different. Therefore $\beta_{\text{loc}}$ should be close to the value determined in the previous study when the current density was close to its diffusion limited value. Table I shows that this, too, is correct.

In summary, we have studied the evolution of the surface roughness for Cu films electrodeposited on microelectrodes. The roughness was always greater nearer the edge, where growth is more rapid, than at the center. However, the scaling exponents were the same for both regions, as is the constant of proportionality relating $w_{\text{sat}}$ to $t'^c$. This means that the roughness near the edge and at the center developed along the same path. Furthermore, despite the non-uniform current distribution at the microelectrode, the values of the scaling exponents were consistent with those measured in an earlier study of Cu electrodeposition on large-area electrodes, and thereby reinforce its conclusions that $H$ and $\beta$ do not depend on the electrolyte concentration or current density, and $\beta_{\text{loc}}$ depends only on the ratio of the current density to its diffusion-limited value.

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References