Atomic Force Microscopy Examination of Cu Electrodeposition in Trenches

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Electrodeposition of copper in trenches with several acid cupric sulfate electrolytes containing benzotriazole (BTA), 4,5-dithiaoctane-1,8-disulfonic acid (SPS), polyethylene glycol (PEG), or chloride (Cl) has been probed by in situ atomic force microscopy (AFM) and ex situ scanning electron microscopy (SEM). The two techniques provide complementary information. A series of AFM images reveals dynamic morphology changes of deposits and trenches during open-circuit dissolution and electrodeposition. Analysis of these AFM images shows vertical and lateral growth of deposits in addition to cross-sectional profile evolution. The grain size analysis obtained from AFM images has been correlated with structures observed in cross-sectional SEM images. While there is a good correlation between grain size and overpotential observed with AFM, this correlation does not extend to the interior structures observed with SEM. Different additives are found to influence growth with behavior ranging from clear conformal growth with BTA to nascent superfilling with SPS + PEG + Cl−.

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The recent development of electrodeposition technology to deposit Cu for use as the interconnect material in microelectronic devices has led to dramatically increased interest in Cu electrodeposition. Cu has a number of advantages over physical vapor deposition (PVD) Al that it replaces. In particular, Cu exhibits low resistivity, high electromigration resistance, and amenability to dual damascene processing.1-3 The electromigration resistance of the plated Cu is orders of magnitude better than that of the Ti/AICu/Ti system it replaces.3

Cu electrodeposition exhibits a number of advantages over PVD or chemical vapor deposition (CVD) processes. First, Cu electrodeposition is a very inexpensive process, estimated to be some 60% cheaper than a putative CVD method.2 Second, electroplated Cu exhibits large grains, resulting in longer electromigration lifetimes relative to CVD Cu.4,5 Finally, a well-tuned electroplating process can fill the high-aspect-ratio structures that are important in deep submicrometer dual damascene architectures.2 The high-aspect-ratio structures are filled via a process known as “superfilling” wherein deposition at the bottom of a trench is enhanced relative to that occurring at the top.6 This enables filling of submicrometer damascene structures without defects and produces void-free and seamless deposits inside lithographically defined cavities with vertical walls.1,3,7-9

The advantages attendant to super-fill Cu electrodeposition require the use of additives, trace amounts of selected inorganic and organic molecules, in the plating bath. In particular, the very desirable superfilling effect occurs only in the presence of certain additive combinations. The effects of additives on electrodeposition of many materials have been examined for years.10 Additives may be involved in (i) grain refinement of the deposit, (ii) polarization of the cathode, (iii) incorporation of additive in the deposit, and (iv) change of the orientation of electrodeposited crystals. In addition, additives may interact synergistically, an effect of relevance to grain refinement of the deposit, (i) polarization of the cathode, (ii) incorporation of additive in the deposit, and (iv) change of the orientation of electrodeposited crystals. In addition, additives may interact synergistically, an effect of relevance to recrystallization phenomena,8,20 apparently promoted by additives directly incorporated in the deposit.

These studies raise questions about the initial stages of Cu electrodeposition in trenches. While inhibition of deposition at trench edges has been postulated in superfilling mechanisms, visual evidence is lacking. The advantages of the in situ experiment to interrogate processes at the solid-liquid interface are well known.23 We have previously used atomic force microscopy (AFM) to develop a mechanistic understanding of the role of certain additives in Cu electrodeposition on planar surfaces.24,25 In this paper, we use AFM to examine the electrodeposition of Cu onto well-defined trench structures both with and without plating bath additives and compare these results with SEM images.

Experimental

1H-Benzotriazole (BTA), polyethylene glycol (PEG, ca. average molecular weight 3400), and KCl were purchased from Aldrich while 4,5-dithiaoctane-1,8-disulfonic acid (SPS) was obtained from Raschig. These chemicals were employed as plating additives without further purification. Sulfuric acid (ultrapure), CuSO4·5H2O (Aldrich, 99.999%), and water purified in a Milli-Q system (18.2 MΩ cm−1) were used in all solutions. Unless noted otherwise, the solution for copper deposition in all the experiments was either a solution of 0.5 M H2SO4 and 0.05 M CuSO4 (additive-free solution) or a solution of 0.5 M H2SO4, 0.05 M CuSO4, and the additives. The compositions of additives were (i) 500 μM BTA, (ii) 1 mM SPS, (iii) 1 mM SPS + 1 mM PEG (SPS + PEG), (iv) 1 mM SPS + 1 mM PEG + 1 mM KCl (SPS + PEG + Cl−). The relatively high BTA concentration was used to ameliorate additive depletion effects known to occur with this additive.25

The working electrode consisted of a Si wafer with 2 μm wide by 0.5 μm deep trench grating arrays in 0.5 μm plasma-enhanced tetraethyl orthosilicate (PETEOS)-SiO2. 500 Å PVD tantalum nitride was first deposited on the oxide as a diffusion barrier and adhesion layer, followed by 1000 Å PVD copper to serve as the cathode for electropolating. These films were deposited sequentially on 150 mm wafers, with no vacuum break, by dc magnetron sputtering in a Novellus M2i cluster deposition tool. Deposition conditions were as follows: tantalum nitride: 3 kW, no bias, 2.9 mTorr, 1:1 collimator, 150°C wafer temperature, 35 sccm Ar, 35 sccm N2, Cu: 3.1 kW, no bias, 1:1 collimator, 50°C wafer temperature, 35 sccm Ar.

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The two techniques provide complementary information. A series of AFM images reveals dynamic morphology changes of deposits and trenches during open-circuit dissolution and electrodeposition. Analysis of these AFM images shows vertical and lateral growth of deposits in addition to cross-sectional profile evolution. The grain size analysis obtained from AFM images has been correlated with structures observed in cross-sectional SEM images. While there is a good correlation between grain size and overpotential observed with AFM, this correlation does not extend to the interior structures observed with SEM. Different additives are found to influence growth with behavior ranging from clear conformal growth with BTA to nascent superfilling with SPS + PEG + Cl−.

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Because of their importance in the superfilling process, the role of additives has been examined in detail. Many workers have interrogated the Cu electrodeposition ex situ using scanning electron microscopy (SEM) or focused ion beam (FIB) microscopy7,8,12-20. These studies have shown that certain additive combinations2,21,22 do in-
The geometric area for electrodeposition was ca. 0.64 cm², a number that does not include the area of the vertical sidewalls of the trenches. The sidewalls are estimated to add another 10% to the geometric area at the start of the deposition process. Both counter and reference electrodes were copper wires (99.999%, 0.25 mm diam) cleaned in 50% sulfuric acid followed by rinsing with hot Milli-Q water. The counter electrode was wrapped around the inside of the cell in order to obviate any potential distribution problems.

Deposition was carried out galvanostatically at a current density of either 0.8 or 5 mA/cm² using a galvanostat (EG&G Princeton Applied Research, model 273). Hydrogen evolution was observed at current densities significantly higher than 5 mA/cm². Potentials are reported with respect to the Cu²⁺/Cu redox couple.

AFM studies were performed using a Molecular Imaging, PicoSPM 300, equipped with a 20 μm scanning head. A pyramidal Si₃N₄ tip mounted on a gold-coated 100 μm v-shaped cantilever (manufacturer’s force constant 0.58 N/m, manufacturer’s included angle 35°) was used. Images were acquired in contact mode. Image size was 20 × 20 μm or 10 × 10 μm. Before each deposition step, the AFM scanner was withdrawn by 40 μm to eliminate possible tip effects on the deposition process. The applied force was minimized so as to reduce any disruption of the surface while scanning.

In these measurements, we utilized 2 μm wide trenches with a 4 μm center-center spacing between adjacent features. Trenches narrower than 2 μm could not be interrogated due to the finite radius of the tips used here. Narrower trenches yielded images representing a convolution of the feature shape with that of the tip because the included angle of the tip makes the tip blind to angles steeper than itself. For 2 μm wide trenches, the images clearly reveal the shape and depth of the trench, but with slanting sidewalls showing the effect of the tip. We note that 2 μm wide and 500 nm deep trenches exhibit aspect ratios smaller than that deemed optimal for observation of the superfilling effect, and that higher aspect ratio features could in concept be imaged with sharper tips.26-28

After Cu deposition, the wafer was cleaned in isopropyl alcohol and cleaved perpendicular to the trench direction to expose the Cu structure within the trench. Scanning electron microscopy (SEM) characterization of the microstructure of the electroplated copper film was made using a Hitachi S4700 instrument.

Results

Dissolution of PVD Cu at open circuit.—Prior to performing electrodeposition measurements, we examined the stability of the PVD copper seed layer in electroplating baths containing the additive combinations examined in this paper. Figure 1 shows a series of in situ AFM images taken immediately following immersion of the sample into solution and then 50 min following immersion at open circuit. The additives fall into two categories. In solutions containing 500 μM BTA comparison of before and after images revealed no change in the shape of the trench. This behavior is expected, as BTA is a well-known corrosion inhibitor for Cu²⁺/Cu redox couple. Not surprisingly, BTA exhibits an overpotential nearly 200 mV greater for Cu electrodeposition under similar conditions than any of the other additives considered. All the other additive combinations fall into the second category wherein the PVD copper layer is unstable and dissolves after immersion. This effect has been noted previously.6 Figure 1c and d show the change in the PVD Cu seed layer after 50 min immersion into a solution containing 1 mM SPS. Figure 1d shows a much rougher surface, exhibiting pits and other inhomogeneities. That corrosion occurs at open circuit in solutions containing SPS is an indication that SPS does not passivate the surface to the same extent as does BTA. The dissolution of copper seed layer was also observed in the other solutions examined here, including additive-free, 1 mM SPS + PEG, and 1 mM SPS + PEG + Cl⁻ solutions. The rate of dissolution was not observed to vary appreciably between these different additives.

Morphology changes during electrodeposition-AFM images.—We followed the change in morphology of a 2 μm wide × 0.5 μm deep trench during the course of the electrodeposition process. Figure 2 is a series of AFM images showing the filling of trenches with Cu in the presence of 500 μM BTA solution as a function of charge using a current density of 5 mA/cm². Cu deposition was continued until a charge of 12 C had been passed, at which
point the images did not reveal any further development of electrodeposition microstructure. 12 C corresponds to an equivalent thickness of ca. 6 μm.

Figure 2a is an AFM image of the trench prior to electrodeposition. As charge is applied to the sample, Fig. 2b-e show that electrodeposition inside the trench catches up with that growing on the terrace next to the trench. After passage of 8 C, the trench is visible as only a slight indentation in the Cu-covered surface.

In order to elucidate the influence of current density on microstructure evolution in the trench, we examined deposition using different current densities. Figure 3 shows a comparison of two systems (additive-free and 500 μM BTA) as a function of current density. Figure 3a and b are the images of the deposits after passing 2.0 C with current densities of 0.8 and 5 mA/cm², respectively. The images obtained by applying low current density display larger grain size and exhibit an apparently lower nucleation density than the images obtained using high current density. The images also show that for the additive-free solution, considerably less charge is required at low current density before the Cu deposited in the trench catches up with that deposited on the terrace above the trench. The trench filled using low current density in BTA-containing solution

Figure 2. Images of copper deposits obtained from 500 μM BTA solution (a) before deposition, and (b) after 2.0, (c) 4.0, (d) 6.0, and (e) 8.0 C.

Figure 3. Images of copper deposits obtained from (a) additive-free solution at the current density of 0.8 mA/cm², (b) additive-free solution at 5.0 mA/cm², (c) 500 μM BTA solution at 0.8 mA/cm², and (d) 500 μM BTA solution at 5.0 mA/cm².
also appears to have caught up with deposition on the terrace above the trench to a greater extent than that accomplished with high current density for the same charge passed. However, higher current densities are likely more relevant to the actual industrial process.

Figure 4 shows a series of images of Cu deposits obtained with five different additive systems after passing 2.0 C with a current density of 5.0 mA/cm². All of the deposits exhibit filling in of the trench relative to the bare surface shown in Fig. 2a. However, the deposits exhibit differing degrees of roughness. For deposition from the BTA-containing solution, copper grains evident both in the trench and on the terrace are small and numerous. We note that these features might not necessarily be grains in the crystallographic sense. In the case of additive-free, SPS, and SPS+PEG solutions, the surface is rougher and the grains are larger. These deposits exhibit minor differences relative to each other. However, deposition from the SPS+PEG+Cl⁻-containing solution evinces a filling action very different from the others. The deposits are quite rough, and the trenches are almost completely filled after passing the same amount of charge. This illustrates that there is considerable literature describing recrystallization of Cu electrodeposits, especially those obtained from SPS+PEG+Cl⁻-containing solution. We obtain SEM images at time scales short enough after Cu deposition so that recrystallization was not an issue.

Table I. The results of the reduction overpotentials of different systems with respect to the Cu²⁺/Cu redox couple.

<table>
<thead>
<tr>
<th>System</th>
<th>Current density (mA/cm²)</th>
<th>Overpotential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive-free</td>
<td>5.0</td>
<td>−173</td>
</tr>
<tr>
<td>With 500 µM BTA</td>
<td>5.0</td>
<td>−419</td>
</tr>
<tr>
<td>With 1 mM SPS</td>
<td>5.0</td>
<td>−216</td>
</tr>
<tr>
<td>With 1 mM SPS + PEG</td>
<td>5.0</td>
<td>−227</td>
</tr>
<tr>
<td>With 1 mM SPS + PEG + Cl⁻</td>
<td>5.0</td>
<td>−64</td>
</tr>
<tr>
<td>Additive-free</td>
<td>0.8</td>
<td>−34</td>
</tr>
<tr>
<td>With 500 µM BTA</td>
<td>0.8</td>
<td>−256</td>
</tr>
</tbody>
</table>

*a The data were reported at 2.0 C.*
nuclei in the trench relative to the low-current-density deposit. The deposits obtained with low current density evince a columnar growth pattern which is known as a field-oriented texture (FT) type, in which crystals grow by two-dimensional nucleation followed by growth with constant grain diameter in all deposition areas. However, with high current density, the morphology appears to make a transition in type at a depth corresponding to a charge of around 6 C. Below the transition point, the deposit appears to be of the unoriented dispersion (UD) type, in which three-dimensional nucleation occurs. Above the transition point, UD-type texture is changed to FT-type texture with larger grain size.

The SEM images show that additive identity strongly controls the morphology of the deposit. In the additive-free case (Fig. 5c) obtained after passage of 8 C, the image shows a plate-like growth known as a basis reproduction (BR) structure in which the Cu crystallites are obtained by two-dimensional nucleation followed by growth in all dimensions. The image also shows the presence of void areas, especially in the vicinity of the trench. Some of these void structures may be due to imperfect adhesion of the deposit to the substrate following the cleavage required to make the SEM sample. The void structure may also have been generated during electrodeposition and be intrinsic to the Cu deposit.

Incorporation of SPS into the plating bath leads to a completely different morphology, as shown in Fig. 5d, which was obtained following passage of 10 C at 5.0 mA/cm². The image shows a deposit with characteristics intermediate between the field-oriented and basis-reproduction (BR-FT) type. Addition of PEG to the SPS solution gives rise to a deposit (Fig. 5e) that is changed again and evinces a more nearly FT structure. Finally, inclusion of Cl⁻ in the bath changes the deposit yet again (Fig. 5f), leading to a BR-type structure. In this case, the grains are much bigger than those obtained from the other solutions.

The BTA, SPS, and SPS + PEG-containing solutions all give rise to electrodeposit structures that feature voids and other defects, as observed by SEM images. These voids are possible sites of additive inclusion. The size of these defects is correlated with the overpotential that, in turn, is related to the solution composition (Table I). Higher overpotential reduces the defect size. For example, comparing Fig. 5b (overpotential = 419 mV) with Fig. 5f (overpotential = 64 mV), the apparent grains are larger in the latter image.

Analysis

Section analysis.—Figure 6 shows the change in cross-sectional profiles derived from the AFM images as a function of charge for five different systems obtained using a current density of 5.0 mA/cm². Each cross-sectional profile shown in Fig. 6 is the average of all of the 512 scan lines of the 10 × 10 μm image. For clarification, the z scale value at x = 1 μm is set to 0 nm for each cross section. The profiles show that the development of trench morphol-ogy depends strongly on the additive with different rates of plating at the bottom and along the sidewall of the trenches.

This section analysis provides considerable insight into the types of profile evolution occurring in Damascene plating. In conformal plating, copper is deposited equally at all points. Therefore, the depth of trench will not change until the flat bottom becomes triangular in shape. In superfilling conditions, the deposit in the bottom of the trench is thicker and the deposit at the top of the trenches is relatively thinner. The depth of the trench, therefore, decreases as a function of coverage before the cross section becomes triangular.

The cross-sectional profiles obtained from the solution containing BTA displays typical conformal plating evolution without changes of depths, whereas the profiles from the SPS + PEG + Cl⁻ solution shows superfilling plating with decrease in depth. For additive-free, SPS, and SPS + PEG solutions, the changes of the profiles seem to indicate a plating action intermediate between superconformal and conformal.

Roughness analysis.—Quantitative measurement of surface roughness is obtained from the standard deviation of the perpendicular...
lar surface variation, $\xi$, also known as the root mean square (rms) height of the surface. $\xi$ is obtained over the entire image and so initially reflects the roughness due to the presence of the trench in the image. As the deposit fills the trench, the roughness should decrease.

Figure 7 shows the change of $\xi$ for the five systems as a function of charge. At the early stages, the value of roughness observed reflects the trenches. The value of $\xi$ saturates after the trenches are filled in and flat surfaces are formed. The saturated values indicate the roughness of deposits. The order of the value of roughness is SPS $\rightarrow$ PEG $\rightarrow$ additive-free $\rightarrow$ SPS + PEG $\rightarrow$ SPS $\rightarrow$ BTA.

Grain size analysis.—Electrodeposits featuring large grain sizes imply the presence of a substantial lateral growth mechanism due to the small grain size of the seed layer. The grain sizes and total number of grains in the images shown in Fig. 2 were investigated quantitatively in the following manner. We note again that these features are not necessarily crystallographic grains but are certainly nuclei resulting from electrodeposition. The morphology is displayed by measuring $z$ height at each $x$ and $y$ coordinate in the AFM image. The number of points of the same $z$ height was determined. At different amounts of charge passed, a histogram as a function of height was obtained. The histograms for the additive-free, BTA, and SPS $\rightarrow$ PEG + Cl$^-$ systems are shown in Fig. 8. For clear comparison, the depth of the largest peaks was set to 0 nm. The largest two peaks at the charge of 0 C correspond to height points from the top and bottom layers of the bare copper trenches. The region between the two peaks reflects the sidewalls of the trenches. The spacing between the two peaks indicates the depth of the trenches, while the width of the peaks shows the roughness of deposits in and out of the
The full width at half maximum (fwhm) from the peak in the histogram corresponding to the area above the trenches was used to set a threshold to visualize the grains. The height below half maximum is displayed in black as shown in Fig. 9. Figure 9 reflects grains of electrodeposits on the top of trenches for five systems after passing 2.0 C with a current density of 5.0 mA/cm². Different grain sizes and numbers of grains are shown clearly in Fig. 9. The order of the average grain size obtained from those solutions is SPS + PEG + Cl⁻ > additive-free > SPS > SPS + PEG > BTA, as summarized in Table II. The number of nuclei density and the deposit size depends on the composition of electroplating solution. By correlating the roughness \( \xi \) values obtained previously and the grain size, the electrodeposits containing SPS + PEG + Cl⁻ grow laterally and vertically to a greater extent than the deposits obtained from the other additive mixtures.

Power spectral density analysis.—Unfilled large trenches and small electrodeposits on the large features can produce the same roughness value as that obtained from large electrodeposits and smooth filled trenches. Power spectral density (PSD) is a method for characterizing each surface’s feature frequency or wavelength. For more complex surfaces, it would be helpful to know which wavelengths occur most often and which impart the greatest influence or power to the surface topography. The PSD is obtained by calculating the fast Fourier transform (FFT) of the autocovariance function or by calculating the square of its Fourier transform. The frequency distribution for a digitized profile of length \( L \), consisting of \( N \) points, \( z_j \), sampled at intervals of \( d_0 \) is approximated by

\[
\text{PSD}(f) = \frac{d_0}{N} \sum_{j=1}^{N} |z_j e^{-i2\pi f(j-1)d_0/Nd_0}|^2
\]

where \( i = \sqrt{-1} \), and frequencies, \( f \), range from 1/L to N/2/L. In our case, \( L = 20 \mu m \) and \( N = 512 \). The wavelength is the inverse of frequency. The maximum of the wavelength in the images is 20 \( \mu m/cycle \) and the minimum is 0.078 \( \mu m/cycle \). The power, \( P \), which is obtained from squaring the FFT of the image, is used to derive 2D isotropic PSD as follows

\[
2D \text{ isotropic PSD} = \frac{P}{2\pi f(\Delta f)}
\]

Here, \( \Delta f \) is the difference in frequencies which in this case is \( 5 \times 10^{-5} \) nm⁻¹.

Figure 10 shows power spectral density plots for three systems. In the case of a BTA-containing solution, many distinct peaks are shown. The peaks at 4 and 2 \( \mu m/cycle \) arise from the trenches. In the solution containing SPS + PEG + Cl⁻, the trench-induced periodicity of the surface is lost, suggesting that the roughness calculated previously is not associated with the trenches as it might be in the BTA case. In an additive-free solution, an intermediate growth pattern results as discussed previously.

**Comparison between SEM and AFM cross sections**.—We used SEM to examine the effect of scanning the Cu electrodeposited with the AFM. In contact mode AFM, the tip is in contact with the surface, and may remove or alter soft layers in contact with Cu. We grew the electrodeposited with the tip withdrawn from the surface and then stopped deposition to interrogate with the AFM. The consequences of this interrogation are shown in Fig. 11a, which is an SEM image for an area scanned by the AFM tip. The overall morphology of this cross section is similar to that found in areas not scanned by the AFM. However, the presence of discrete layers is clearly noted in the image. These layers correspond to the material deposited between AFM interrogation steps. Note that SEM images obtained from areas absent AFM scanning do not show this discrete pattern, even though they were grown in the same way. The origin

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**Figure 8.** Histograms as a function of charge passed obtained from (a) additive-free solution, (b) 500 \( \mu M \) BTA solutions, and (c) 1 mM SPS + PEG + Cl⁻ at a current density of 5 mA/cm². (○), (△), and (▼) denote histograms obtained at 0, 2.0, and 4.0 C, respectively.

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The roughness obtained by scaling analysis is a convolution of the roughness intrinsic to the trenches and that developing from electrodeposits. From these histograms, the roughness of the copper electrodeposits can be investigated excluding the intrinsic trench contribution. The roughness of top and bottom layers can be explored separately by measuring the width of the two peaks.

In Fig. 8b, obtained with BTA as the additive, the width of the peak associated with the top of the trench does not change as a function of coverage. This indicates the electrodeposits are very flat. The disappearance of the peak associated with the bottom of the trench in this plot implies that the bottom of the trench is no longer flat and reflects the evolving trigonal shape seen in the section analysis. The behavior of the histogram obtained from the solution containing SPS + PEG + Cl⁻ shown in Fig. 8c is different from that obtained with BTA. After passing 2.0 C, the two peaks become much broader and the maximum of the bottom layer peak shifts to smaller values. This means that the electrodeposits on both the top and bottom layer of the trenches are very rough and the depth of the trenches decreases. The peaks for the additive-free solution show a pattern intermediate between those with BTA and SPS + PEG + Cl⁻ as shown in Fig. 8a.
of the discrete layering likely arises from interference by the scanning AFM with adsorbed layers of additive on the surface during the interrogation step.

Analysis of the image provides some additional information about the AFM imaging. AFM images were obtained 0.0, 0.5, 1.0, and then at 1.0 C increments. Assuming a current efficiency of 100% and a uniform Cu layer, each 0.5 C of charge is then calculated to correspond to a Cu deposit layer 287 nm thick. Figure 11b shows the result of offsetting the AFM cross-sectional images for 0.5, 1.0, and 2.0 C by 574 nm/C. The correspondence with the SEM image shown in Fig. 11a is quite good. In particular, the calculated depth of the deposit at 2.0 C is 1148 nm, while the SEM image gives a depth of 1150 ± 20 nm. The SEM/AFM comparison also reveals issues at low Cu coverage with sidewall imaging by AFM, as is

Table II. The grain size and the number of grains.

<table>
<thead>
<tr>
<th>System</th>
<th>Average grain size (nm²)</th>
<th>Number of grains</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive-free</td>
<td>31,480</td>
<td>117</td>
</tr>
<tr>
<td>With 500 µM BTA</td>
<td>2877</td>
<td>1928</td>
</tr>
<tr>
<td>With 1 mM SPS</td>
<td>17,140</td>
<td>414</td>
</tr>
<tr>
<td>With 1 mM SPS + PEG</td>
<td>9726</td>
<td>561</td>
</tr>
<tr>
<td>With 1 mM SPS + PEG + Cl⁻</td>
<td>36,870</td>
<td>119</td>
</tr>
<tr>
<td>With 500 µM BTA*</td>
<td>9999</td>
<td>627</td>
</tr>
</tbody>
</table>

* The data were reported at 12.0 C, other data were reported at 2.0 C.

Figure 9. Images of grains on the top of trenches obtained from (a) additive-free, (b) 500 µM BTA, (c) 1 mM SPS, (d) 1 mM SPS + PEG, and (e) 1 mM SPS + PEG + Cl⁻ solutions after passing 2.0 C at a current density of 5.0 mA/cm².

Figure 10. Power spectral density is plotted for each solution after passing 4.0 C.
evident in a comparison of the circled areas in Fig. 11a and b. Alternatively, the top corners of the trenches and the terrace areas both in and out of the trench appear to be well imaged. At higher coverages, the SEM and AFM cross sections are nearly identical. Intermittant rastering with the AFM tip during electrodeposition provides a way to induce structuring into the Cu structure that with appropriate development may lead to a way to introduce other kinds of striation into the deposit.

Discussion

In this paper we used AFM, SEM, and electrochemical methods to address a number of issues relevant to electrodeposition in trenched microstructures. The results and analysis presented provide insight into the way in which additives control the filling of these trenches by the Cu electrodeposit. The additive makeup also strongly influences the overpotential at which plating occurs and the number and distribution of nuclei in the process. From analysis of AFM and SEM images, insight into the particular growth mechanism directed by the additives can be obtained. Finally, the results speak to the correlation of AFM and SEM methodologies.

Perhaps the major result of this study is the demonstration that a surface analytical method, contact mode AFM, can provide information about the fill characteristics of Cu electrodeposited from solutions of different additive combinations.

Comparison of AFM and SEM-derived information.—One advantage accruing to AFM over the more conventional SEM measurement is that the AFM can provide high-resolution lateral and vertical information in one image, whereas a multitude of images are required to obtain the same information with SEM. This additional information is useful here, because the AFM provides information about the development of grains as a function of applied potential. Use of the SEM has previously been limited only to the evolution of the Cu electrodeposit in the trenches. However, there are clearly different topographical features associated with trench filling that are seen with the AFM. Grains with sizes only several tens of nanometers in width are hard to ascertain in SEM images. The AFM can also be used to monitor the evolution of trenches and deposit as a function of charge. The histogram analysis gives insights into the vertical growth of the deposit and the evolution of trenches. The AFM also distinguishes between cases having similar cross sections but different grain sizes, as is the case in Fig. 3c and d. The equivalent cross-sectional SEM images, Fig. 5a and b, also evince differences, but these are somewhat harder to see.

Correlation between electrochemical, SEM, and grain size measurements.—The analysis shows clearly that for a constant current density, the overpotential can be related to both the grain size as determined by AFM and inner structures as determined by SEM. We showed that higher overpotential makes for smaller grain size, a result described previously only for the additive BTA on flat surfaces. The overpotential does not depend on deposit thickness. However, there is also a correlation between overpotential and the inner structure of the deposit as determined by SEM. The deposit structure evolves as FT-UD > FT > BR-FT > BR as the overpotential decreases. This suggests that smaller grains may produce UD or FT structures. These FT or UD structures feature voids and other inhomogeneities that may be sites of additive inclusion. Indeed, secondary ion mass spectroscopy (SIMS) results suggested the inclusion of BTA in what we now know are FT-UD or FT structures. This inclusion may be the origin of the high resistivity found by Moffat and co-workers in this system.

BTA.—The deposits grown from BTA-containing solution yield the highest overpotential (Table I), lowest roughness (Fig. 7), highest nuclei density (Fig. 9), smallest average grain size (Table II), but poor ability to fill the trenches (Fig. 10). The inhibiting organic layer formed on copper surfaces by this additive makes the overpotential high. In the initial stage (below 6 C), the high overpotential suppresses lateral and vertical growth and consequently creates a number of nucleation sites. The lateral diffusion length of copper ion on the surface suggested by grain size analysis of the AFM image (Fig. 9b) is small.

The cross-sectional SEM image (Fig. 5b) shows consistent results with numerous small grains showing UD texture-type growth structure. In this stage, surface relaxation, in which particles (Cu adatoms) on the surface move and fill up recesses so as to produce a flat surface, is supposed to contribute to the growth mechanism. The flat surface gives a typical conformal plating action (Fig. 6b). The cross-sectional SEM image (Fig. 5b) shows the transition of the types of growth structure from UD type to FT type with larger grains. The incorporation or inclusion of molecules into the metal matrix during deposition is a process that is believed to further account for additive consumption. In our previous results, SIMS measurements of the copper deposits for BTA-containing solution show that a significant amount of organic material is incorporated in the deposits, implying a consumption of BTA.

In our previous results, big, pyramidal features were observed following passage of a certain charge. These pyramidal features were associated with depletion of additive, due to additive incorporation in the deposit. In this experimental system, we used a higher concentration of BTA so that depletion was not significant enough to promote the pyramidal features. Over the course of deposition, the overpotential decreased from −0.419 V (at 2.0 C) to −0.204 V (at 12.0 C) due to a decreased inhibiting layer. Lower overpotential makes grains wider and rougher. Grain size analysis reveals that average grain size and number of grains are changed from 2877 nm² and 1928 at 2.0 C to 9999 nm² and 627 at 12 C, respectively. As more charge is applied to the sample, lateral growth makes more contribution at higher charges. SPS + PEG + Cl⁻.—The cross-sectional SEM images of deposits grown from SPS + PEG + Cl⁻ show large grains with a BR-type structure. The presence of these large grain boundaries suggests that diffusive mechanisms transporting Cu onto growing grains are operative and that lateral growth is a factor. The lower overpotential found here relative to the other solutions may admit longer diffusion of particles on the surface before reduction and incorporation. SPS and SPS + PEG.—The deposit grown from SPS reveals a BR-FT structure while the SPS + PEG-containing solution gives rise to a FT-type deposit. These different structures must reflect different 3D growth modes for the deposit. Even though the surface morphologies are similar with similar overpotentials, the identity and combination of additives alters the internal deposit structures. We suggest that different internal structures arise from differences in the mode and mechanism of additive incorporation in the deposit, as deposits obtained from SPS + PEG feature enhanced C content relative to those formed from SPS alone. The SEM reveals abundant voids and defects, which may be sites of additive incorpor-
ratiom. The origin of these voids may be imperfections arising from the lack of relaxation, possibly inhibited by incorporated additive. It is apparent that overpotential alone does not control the structure of the Cu electrodeposit but is certainly a major contributor.

Conclusion

This work shows that some insight into the growth mechanism of Cu electrodeposits in trenches can be obtained from AFM images. The AFM can follow the deposition of Cu into trench structures under potential control. Analysis of these images in terms of cross-sectional profile evolution, roughness, and change in depth of trenches and grain size provides insight into the way in which Cu grows under conditions of different additive compositions. A close correlation of results is found in cases where the AFM and SEM cross sections can be measured independently at the same place on the surface. Appropriate analysis of these images shows different behaviors of Cu deposit growth from different additive solutions. This behavior ranges from clear conformal growth with BTA to nascent superfilling with SPS + PEG + Cl\textsuperscript{−}. The AFM-derived insight about growth mechanism can be combined with that from cross-sectional SEM. In some cases, notably those involving BTA and SPS + PEG + Cl\textsuperscript{−}, there is a good correlation between the two microscopies. However, in others, this correlation appears lacking. We suggest that the degree of additive incorporation in the deposit is then important.

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