Electrocrystallization Behavior of Copper Electrodeposited from Aqueous Sulfuric Acid with Thiourea and Chloride Additives

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Copper was electroplated from cupric sulfate-sulfuric acid solutions with various concentrations of thiourea and chloride ions. The microstructures of deposits were analyzed by optical microscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD results indicated that the most preferred orientation of the copper deposits was (220) when thiourea concentrations were greater than 5 ppm. However, the preferred orientation changed obviously when chloride ions were added together with thiourea, moreover, the grain type of the deposit changed from columnar to equiaxed. TEM images showed considerable twinning in copper plated from solutions containing less than 1 ppm thiourea. Grain sizes of copper deposits decreased when higher concentrations of thiourea were added to the plating bath, together with chloride ions.

Introduction

In industrial copper electroplating, various additives such as thiourea and chloride ions are added, at ppm (mg/L) concentrations, to the acidic sulfate plating bath, to improve the properties of copper deposits. The crystallographic orientations and surface morphologies of copper deposits have been reported and additives such as thiourea and chloride ion, shown to co-deposit with copper, changing the properties of copper deposits. O’Keefe et al. \cite{1} used SEM and XRD to determine surface morphologies and crystallographic orientations of copper deposits. Maher et al. \cite{2} found thiourea it could act as mediator and brightness agent and has no leveling ability for copper deposit. Pradhan et al. \cite{3} showed that chloride ions affected the crystallographic orientations and morphologies of copper deposits. It was suggested that adsorption of chloride ions changed the preferred growth plane. Carneval \cite{4} found that the anion could be a complex former and even co-deposited with cupric ion during copper electroplating. Although the effect of adding thiourea to copper plating baths has been reported extensively \cite{5-11}, the binary effect of thiourea and chloride ion additives has not been investigated fully.

The objectives of the research for which results are reported below, was to determine the combined effects of thiourea and chloride ions on the electrocrystallization behavior and surface morphologies of copper electrodeposits, using XRD to analyze the crystallographic orientations and optical microscopy (OM) and transmission electron microscopy (TEM) to study their microstructures.
Experimental

A rotating cylinder electrode (RCE), which was fabricated from pure titanium (99.5 wt%, Grade 2) with an exposing area of 1 cm$^2$ (8.4 mm in diameter and 4 mm in length), was used as the cathode in all electroplating experiments. A conventional copper sulfate-sulfuric acid bath was used, comprising CuSO$_4$·5H$_2$O (90 g/l) and H$_2$SO$_4$ (120 g/l) containing 1 to 8 ppm thiourea and 20, 40 or 80 ppm chloride ions. The copper electroplating was conducted at a constant current density of 0.7 A/cm$^2$ at 53 ± 0.5 °C for 135 seconds to obtain a copper deposit with a thickness about 35 µm.

The rotation speed of the RCE was kept 2000 rpm with a rotating disk electrode controller (EG&G RDE 0001). The three-electrode electrochemical cell contained a platinized Ti-mesh counter electrode and Ag/AgCl$_{\text{sat.}}$ reference electrode. The Ti surface of the RCE was mechanically ground with 1200 grit emery paper, cleaned in an acetone bath and dried with a cold air blaster. After electroplating, the copper deposit was carefully peeled from the Ti cathode, cleaned ultrasonically in an acetone bath, and then dried for further study.

The metallographic cross sections of the copper deposits were examined by optical microscopy. Samples about 15 mm long and 5 mm wide were taken, mounted in epoxy, milled by sand paper, polished by diamond paste, and immersed in the etchant consisted of 98 % NH$_4$OH + 2 % H$_2$O$_2$ about 5 seconds to reveal their microstructures. The crystallographic orientations of copper deposits were analyzed by X-ray diffraction. The microstructures of the copper deposit were also examined with transmission electron microscopy (TEM, Jeol 2000FX). The TEM samples were prepared using a twin-jet electrochemical cell (Fischion Instruments, inc.) in which the polishing electrolyte was 40% H$_3$PO$_4$ + 60% H$_2$O. 5 V was applied between the specimen and a platinum counter electrode, until a tiny hole was produced in the middle of the specimen, around which the sample was so thin that could be examined and analyzed with TEM.

Results and Discussion

Crystallographic Orientation

The XRD analyses of copper deposits electroplated with various concentrations of thiourea and chloride ions are listed in Table 1. Diffracted intensities of these planes of copper deposits was compared with the diffraction result of pure copper powder, whose orientation was random; therefore, the preferred orientation of copper deposits could be determined. The scatter intensity of the copper powder showed the major preferred orientation was (111). For copper deposits without addition of thiourea and chloride, the order of preference crystal planes was major (220) and minor (111), (200). The major orientation remained at (220) for thiourea concentrations $\leq$ 8 ppm; however, the intensity of minor orientations (111) and (200) decreased with increasing thiourea concentration. For thiourea concentrations in the plating bath $>$ 5 ppm, the preferred growth of (220)-plane of the copper deposit could be observed.

The effect of both thiourea (TU) and chloride ions on crystallographic orientation of copper deposits is also listed in Table 1, indicating that the additives obviously affected the crystallographic orientations of copper deposits. The major orientation of copper
deposits was the (220) plane and then minor orientations of (111) and (200) planes, when lower concentrations of thiourea (1 ppm) and different concentrations of chloride ion were added together in the plating bath. However, the copper deposits had two major orientations (111) and (220) when higher concentrations of thiourea (8 ppm) and higher concentration of chloride ion (80 ppm) were added together in the plating bath.

### TABLE I. XRD analysis of copper deposits electroplated with various concentrations of thiourea and chloride ions.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>(111)</th>
<th>(200)</th>
<th>(220)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Powder</td>
<td>100</td>
<td>46</td>
<td>20</td>
</tr>
<tr>
<td>No additive</td>
<td>27.5</td>
<td>15.6</td>
<td>100</td>
</tr>
<tr>
<td>TU 1 ppm</td>
<td>24.1</td>
<td>12.1</td>
<td>100</td>
</tr>
<tr>
<td>TU 5 ppm</td>
<td>9.0</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td>TU 8 ppm</td>
<td>0.0</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td>TU 1 ppm Cl 20 ppm</td>
<td>18.6</td>
<td>13.0</td>
<td>100</td>
</tr>
<tr>
<td>TU 1 ppm Cl 40 ppm</td>
<td>14.7</td>
<td>13.5</td>
<td>100</td>
</tr>
<tr>
<td>TU 1 ppm Cl 80 ppm</td>
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<td>26.9</td>
<td>100</td>
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</tr>
<tr>
<td>TU 8 ppm Cl 80 ppm</td>
<td>100</td>
<td>24.7</td>
<td>100</td>
</tr>
</tbody>
</table>

### Optical Microscopy

Figure 1 shows the cross section microstructures of copper deposits electroplated in the presence of various concentrations of thiourea and chloride ions. For copper deposits with and without 1 ppm thiourea, tilted columnar structures were observed in the cross-section micrograph. However, perpendicular columnar structures predominated in the copper electrodeposited with thiourea concentrations higher than 5 ppm. A surface leveling effect on the deposit was evident for thiourea concentrations higher than 5 ppm, in agreement with the results of Suarez and Olson (8) and Alodan and Smyrl (10), who reported that leveling and brightening of the copper deposit surface could be achieved when electroplating copper in acidified sulfate baths with thiourea additions.

It can also seen that the grains of copper deposits became random and surfaces uneven on addition of 1 ppm thiourea and various concentrations of chloride ion to plating bath. On the other hand, addition of 8 ppm thiourea and various concentrations of chloride ions to the plating bath, caused the grain type to change from columnar to equiaxed; furthermore, the grain size of copper deposits decreased with increasing chloride ion concentration.
Figure 1. Optical microscopic images of copper deposit electroplated in the presence of specified concentrations of thiourea and chloride ions.
Transmission Electron Microscopy

Figure 2 shows the TEM micrographs of copper deposits electroplated from solutions with different concentrations of thiourea and chloride ions. In the micrographs of copper deposits electroplated in the presence of 1 ppm thiourea, extensive twinned structures were evident in the copper deposit, though their concentration decreased significantly with increasing thiourea concentration (≥5 ppm). Some large twin structures were found in copper electrodeposited from solutions containing 1 ppm thiourea and various concentrations of chloride ion. Comparing the twin structures of copper electrodeposited from solutions with thiourea only and thiourea with chloride ions, the former were larger in size but smaller in number.

Figure 2. TEM micrographics of copper electrodeposited from solutions with the specified concentrations of thiourea and chloride ions.
It should be mentioned that twin structures almost vanished in copper electrodeposited in the presence of 8 ppm thiourea and various concentrations of chloride ion; furthermore, the grain sizes of copper deposits were much smaller than those electroplated from solutions with lower concentrations of thiourea.

Conclusions

XRD results indicated that the preferred orientation of copper deposits was (220) when thiourea concentrations in the plating bath were greater than 5 ppm, which also resulted in leveling and brightening of deposit surfaces. The preferred orientation of copper deposits changed obviously when chloride ions were added together with higher thiourea concentrations. Moreover, the grain type of the deposit changed from column to equiaxed when chloride ions were added together with higher concentrations of thiourea. Large numbers of twins were evident in TEM images in copper electrodeposited from solutions with 1 ppm thiourea, but the numbers decreased significantly when thiourea concentration were greater than 5 ppm. Grain sizes decreased when copper was electrodeposited from solutions containing chloride ions and to which 8 ppm thiourea had been added.

References