The Effect of Hydroxy Ethyl Cellulose (HEC) and Chloride Ions on the Surface Morphology and Mechanical Characteristics during Copper Electrodeposition

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The effect of additives on the surface morphology and mechanical characteristics during copper electrodeposition on the polyimide (PI) film was investigated. Two kinds of additives such as hydroxy ethyl cellulose (HEC) and chloride ions were used in this study. Electrodeposition was carried out with the constant current density of 200 mA/cm² for 68 seconds. Electrochemical experiments, in conjunction with SEM, XRD, AFM and four-point probe, were performed to characterize the morphology and mechanical characteristics of copper electrodeposited in the presence of the additives. The minimum surface roughness of copper deposit was obtained when deposited with 10 ppm of chloride ions. The minimum value of surface roughness (rms value) was 97.05 nm. And the optimum amount of additives to improve the electromigration resistance and ductility of the deposit was a combination of 1 ppm HEC and 10 ppm chloride ions. [doi:10.2320/matertrans.MRA2006326]

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1. Introduction

Flexible printed circuit board (FPCB) is distinguished from rigid printed circuit board by its functionalities that are particularly useful for applications that require connection to moving and bending parts, circuit boards mounted in a 3-D structure and high density interconnects. With the design flexibility and space efficiency, FPCB is used in a wide variety of high-tech hardware such as computers, telecommunication equipments, medical devices, and electronic instruments for air and space flight. The base film materials of FPCB used to make interconnections between the traces are polyimide, polyester, and fiber glass reinforced epoxy. Among them, polyimide film is most commonly used due to its excellent resistance to chemicals, high thermal stability, low dielectric constant, and super flexibility. The recent trend of compactness, smallness and lightness of electronic elements has fueled the use of thin film process for the manufacture of FPCB. FPCB is fabricated by deposition of a thin metal layer on the dielectric material. Therefore, FPCB is composed of multilayers such as metal film/dielectric layer/thin metal layers. Many researches have aimed at increasing the adhesion strength of interfaces between layers. To plate a layer of copper foil on the substrate, various deposition techniques have been used including electrodeposition, CVD, PVD, sputtering, and thermal evaporation. Among these techniques, electroplating is the most commercially important process because it is time-efficient and cost-effective without the need for the vacuum system that is required for sputtering and thermal evaporation techniques. In addition, it facilitates changes in electrolytic composition, the particle size, and deposit thickness by allowing variations of the reaction speed and time at electrodes in response to the required deposition potential.

By adding organic and inorganic additives to an electrolytic solution, a homogenous surface can be achieved. In addition, the crystal size, crystal orientation, ductility and hardness of the deposited films can be adjusted during the electroplating process even while ensuring good composition. These functional effects of additives make it possible to tailor a thin-film deposition to meet a specific end use application by optimizing the electrolytic composition and deposition conditions. If the solution composition and deposition conditions are standardized to optimize the effects, it is possible to mass produce FPCB materials with excellent electrical and mechanical properties.

In this study, the effect of additives such as hydroxy ethyl cellulose (HEC) and chloride ions on the electrical and mechanical properties of copper films electrodeposited on the polyimide (PI) film during copper electroplating was investigated and the surface morphology of copper films was also evaluated.

2. Experimental Methods

2.1 Test Sample

Sputtering and electroplating were performed on 25 μm thick PI films (DuPont’s Kapton H). Figure 1 shows the chemical structure of PMDA-ODA polyimide that consists of 22 carbon atoms, 5 oxygen atoms, 2 nitrogen atoms, and 12 hydrogen atoms for each repeated unit. PI film samples with a size of 2 x 2 cm² were cleaned with acetone and dried at room temperature for six days. For the sputtering of Pt on
the PI films, an ion sputtering technique was used. Ar gas was pumped into the vacuum chamber with an initial vacuum of 0.02 mbar, and the pressure was maintained with an argon atmosphere at a level of 0.06 mbar during deposition. The sputtering was conducted at the condition of 1.5 keV/30 mA. The deposition rate was about 43 nm/min, and the thickness of Pt film was about 130 nm after 5 min. deposition. In the electroplating process, the cathode was constructed using acid resistant tape to allow only a part (area of 1 cm²) of the Pt/PI film to be exposed to the electrolyte. A grid-type Pt (Ametek, USA) plate was used as the anode.

2.2 Electroplating Process

The temperature of the electrolyte was maintained at 65°C (±0.5°C) using a water-jacketed glass beaker of 500 cm³. All the potentials were measured using a reference electrode of Hg/Hg₂SO₄ (+656 mV vs. SHE). The composition of electrolytic solution was Cu 100 g/L + H₂SO₄ 100 g/L and the solution was prepared by mixing CuSO₄·5H₂O and H₂SO₄ with deionized water obtained by a water purification system (Elisio®3, Millipore, U.S.A). The distance between electrodes was maintained at 3 cm throughout the process. The prepared electrolytic solution was agitated with a stirring rate of 100 rpm to increase the mobility of the additives and Cu²⁺ ions. The chloride ion was added with the form of HCl and an average molecular weight of HEC was 1,600,000 to 1,700,000. For the electrodeposition process, an EG&G PAR model 273A potentiostat/galvanostat connected to a microcomputer with the M270 software was used. Electrodeposition was performed under galvanostatic mode with a constant current density of 200 mA/cm², and a 5 μm thick copper layer was formed. Additives were added individually or in combination depending on deposition conditions as shown in Table 1.

Table 1 Kinds and amount of additives used in this study.

<table>
<thead>
<tr>
<th>Additives groups</th>
<th>Cl⁻</th>
<th>HEC</th>
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<tbody>
<tr>
<td>NA</td>
<td>No Additive</td>
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</tr>
<tr>
<td>Cl</td>
<td>C-5</td>
<td>5</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>C-25</td>
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<td>10</td>
</tr>
<tr>
<td></td>
<td>CH-3</td>
<td>10</td>
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</tbody>
</table>

2.3 Analysis

A scanning electron microscope (SEM; JSM-5900, JEOL, Japan) and X-ray diffractometer (XRD; Dmax III-A type, Rigaku Co., Japan) were used to examine the surface morphology and crystal size, and to analyze the phases of the deposited copper film, respectively. Atomic force microscopy (AFM; BioScope, Digital Instruments, U.S.A.) was used in order to characterize the morphological change of the surface of electrodeposited copper film. The thickness of Pt and copper films was measured using an α-step (KLA-Tencor Co., U.S.A). Resistivity of the deposited copper films was measured with a four-point probe (CMT-SR1000N, AIT, Korea). And hardness was measured using a Micro-Vickers hardness tester (MHT-1, Matsuzawa Seiki, Co. Ltd., Japan) at a load of 50 g for 15 seconds using shiny side of the 25 μm thick copper deposit to minimize the possible problems due to the surface roughness and porosity. For each set of data for resistivity and hardness measurements of copper films, five points on two different specimens were used.

3. Results and Discussion

3.1 Micrography

SEM images, obtained during the experiment with the electrolytic solutions in which chloride ions and HEC were applied individually or in combination for 68 seconds are presented in Figs. 2, 3, and 4. As can be seen in Fig. 2, there is not any significant difference in surface morphology between deposited films without additives and those with chloride ions. When deposited with chloride ions, some
crystals exhibited increased size, and micro pinhole was shown at a concentration of 25 ppm chloride ions. Figure 3 represents the surface morphology of copper films with HEC was not significant different from that deposited without additives (NA). However, the synergistic effect of HEC and chloride ions can be seen in Fig. 4. As the amount of HEC increased with a fixed amount (10 ppm) of chloride ions, crystal size distribution was inhomogeneous and large pinholes were formed.

Figure 5 shows SEM micrographs of copper films deposited to a thickness of 25 μm using a Ti foil as the cathode. They were prepared for hardness measurement. As shown in Fig. 5, the micro pinhole significantly increased with the addition of 10 ppm chloride ions. However, micro pinholes disappeared with the addition of HEC.

### 3.2 Mechanical Properties

#### 3.2.1 AFM Measurement

Figure 6 shows AFM images of the 5-μm thick copper film. The overall rms roughness values significantly decreased with the addition of chloride ions compared with those values without additives. The rms values were not significantly changed with the addition of chloride ions up to the amount of 10 ppm. However, the amount of chloride ions increased over 15 ppm, the rms values increased about 13%. Although the addition of HEC with the amount of 1 ppm reduced the rms value, it was again increased with more than 2 ppm of HEC up to about 15%. These results suggested that the surface roughness of copper deposit could be controlled by the amount and combination of HEC and chloride ions. The rms value of copper foil deposited with HEC and 10 ppm of chloride ions was higher than that deposited without additive, and it was increased with the amount of HEC.

#### 3.2.2 XRD Analysis

Figure 7 represents XRD patterns for the surface of copper films deposited with various additives. The intensities of the (111) and (220) diffraction peaks were higher compared with other peaks in the NA group. However, the intensity of the (111) diffraction peak was significantly increased and those of (200) and (220) diffraction peaks were decreased for copper films with the addition of chloride ions, which indicated the preferred crystal orientation. And this trend was most pronounced when 10 ppm of chloride ions were added. These results suggest that electroplated copper could show a higher resistance to electromigration at a chloride ion concentration of 10 ppm.\textsuperscript{14,15}

With the addition of HEC, the intensity of the (111) diffraction peak was a little higher compared with that of the NA group, leading to the preferred crystal orientation. The (111) intensity was highest at an HEC concentration of 1 ppm. The intensity of the (111) and (200) diffraction peaks decreased while that of the (220) peak increased as the amount of HEC increased up to 3 ppm. However, this intensity trend was reversed at the concentrations of more than 3 ppm.

The addition of HEC combined with 10 ppm chloride ions reduced the intensity of the (111) diffraction peak, compared with that of the (111) diffraction peak with chloride ion alone. However, it was still higher than that with HEC alone. This means that the electroplated copper film had a high resistance to electromigration when HEC is added with chloride ions. Electromigration occurred mostly by the grain boundary diffusion, and the circuit layer having a coordination of (111) planes decreased the activation energy for the grain boundary diffusion and thereby decreased the rate of electromigration.\textsuperscript{14,15}

XRD patterns showed that the intensity of the (111) diffraction peak was highest at an HEC concentration of 1 ppm among various HEC concentrations when combined with 10 ppm of chloride ions.
Fig. 6 AFM images of copper surface deposited at various additives for 68 seconds: Here the scale of the vertical range and horizontal range is 1 μm and 10 μm.

Fig. 7 XRD spectra obtained on the surface of electrodeposited copper for various additive compositions.
3.2.3 Hardness Measurement

The surface hardness of copper deposited on the Ti substrate was measured using a Micro-Vickers hardness tester (Fig. 8). Average value of Vickers hardness of the NA group was 52.2, and they were decreased with additives. As mentioned earlier, copper films deposited with chloride ions showed a (111) preferred orientation, and the rms value was the lowest at a concentration of 10 ppm. Vickers hardness value of the deposit with a chloride ion concentration of 10 ppm was 11.15. Although the hardness values of the deposits with HEC were higher than those of the deposits with 10 ppm of chloride ions, they were lower compared with those of the deposits in the NA group. However, there were no significant differences in hardness values with the amount of HEC up to 3 ppm. When added more than 4 ppm of HEC, hardness was increased. And this trend was similar even if 10 ppm of chloride ions were added.

3.2.4 Resistivity Measurement

The resistivity values of the electroplated copper films are represented in Fig. 9. Thin metal films are known to have higher resistivity than bulk samples because of residual resistivity characterized by surface scattering, boundary scattering, impurity, and intergranular defects. The resistivity values of the copper films deposited in this study were higher than the typical value of bulk sample of 1.67 $\mu\Omega\cdot$cm.7,14) The resistivity was increased in films deposited with additives. That of the NA group was 2.051 $\mu\Omega\cdot$cm. The resistivity of films increased to 2.237 $\mu\Omega\cdot$cm with the amount of chloride ions up to 10 ppm. However, the resistivity decreased with the further increase of chloride ions. The increase in resistivity can be explained by reduced grain size, increased defect density, and fine structure.15) In this study, it can be assumed that the high resistivity of the deposit was mainly due to the highly defective structure originated from preferred growth of the close packed (111) grains. And the low hardness value support that the deposit is defective. The resistivity was highest for the deposit with 2 ppm of HEC, and the value was 2.299 $\mu\Omega\cdot$cm. The resistivity decreased as the amount of HEC further increased. When 2 ppm of HEC was added with 10 ppm of chloride ions, the resistivity was highest and the value was 3.821 $\mu\Omega\cdot$cm. The resistivity decreased with further increase of HEC.

4. Conclusion

In this study, copper films were deposited on a Pt/PI substrate using an electroplating technique with additives such as chloride ions and HEC. Results are summarized as follows:

(1) Copper films deposited without additives exhibited high Vickers hardness and surface roughness, rendering them unsuitable for FPCB applications. However, the proper addition of chloride ions and HEC significantly improved the surface properties of the deposition layer, such as low hardness and smooth surface.
(2) A copper deposit with a preferred growth orientation of (111) is important to the resistance to electromigration. The copper films deposited without additives did not exhibit Cu (111) preferred growth, leading to a low resistance to electromigration. Instead, copper films deposited with both chloride ions and HEC exhibited Cu (111) preferred growth. (3) It was found that copper films deposited with HEC alone had low hardness and the electromigration resistance remained unsatisfactory. The optimum amount of additives to improve the electromigration resistance and ductility of the deposit was a combination of 1 ppm HEC and 10 ppm chloride ions.

REFERENCES