Electron Backscatter Diffraction Characterization of Microstructure Evolution of Electroplated Copper Film

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The microstructure evolution of electroplated copper films was characterized by electron backscatter diffraction (EBSD). Special care was taken during the preparation of the cross-sectional specimens and microstructure analysis to obtain reliable results. The film exhibited a columnar grain structure with a large fraction of twin boundaries. Annealing induced normal grain growth and caused many of the general high-angle grain boundaries to be replaced by twin boundaries, possibly by annealing twinning.

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1. Introduction

Copper film is used as a metallization material in microelectronics. The increasing interest in copper films is driven by their large spectrum of applications in printed circuit boards, ultra-large-scale integration (ULSI) metallization, and flexible electronics. The physical, mechanical, and chemical properties of polycrystalline copper films are influenced by their microstructural characteristics, such as their grain size, grain boundary characteristics, and grain orientation. The strengths of metallic films are inherently related to their grain size. Their electromigration performance is influenced by their grain size, grain distribution, grain boundary misorientation and texture. The flexibility or bending fatigue resistance of the copper films used for flexible printed circuit boards is strongly influenced by their microstructure evolution. The texture evolution should be taken into consideration, because the macroscopic behavior of polycrystalline copper films depends on the orientation distribution of the crystallites. The elastic anisotropy of textured copper films can give rise to non-uniform mechanical properties and their grain boundary characteristics are influenced by their texture evolution. The microstructure of copper films grown by vapor deposition or electro-deposition can be changed by heat treatment. The modification of the grain boundary structure of copper films by recrystallization, grain growth, and twin formation during annealing can change their properties and reliability.

The microstructure evolution of copper films can be characterized by several techniques: optical and electron microscopy, focused ion beam (FIB) imaging, and electron backscatter diffraction (EBSD). EBSD provides information on the grain size and morphology statistics and grain boundary characteristics, as well as the crystal orientation of the individual grains. There have been several studies involving the EBSD analysis of copper films, but systematic studies by means of cross-sectional mapping are still lacking. Cross-sectional observation is essential for identifying columnar grain structures of copper films. EBSD measurement only on the film surface does not provide overall information throughout the thickness of the specimens. The cross-sectional EBSD measurement by Panteleon et al. would not be guaranteed because many numbers of the pixels remained non-indexed and the grain morphology was not identified.

In the present study, we carried out a cross-sectional EBSD analysis of electroplated copper films. Special care was taken in preparing the EBSD specimens, in order to avoid any possible artifacts of orientation measurement. A commercial flexible copper clad laminate (FCCL), where copper film was deposited on polyimide (PI) film, was used. The specimens were annealed and the effect of the annealing was investigated. We characterized the grain size and grain boundary characteristics of the as-received and annealed specimens and discussed the mechanism of microstructure evolution.

2. Experimental

2.1 Specimen preparation

The specimen used in this study is a commercial FCCL which is composed of 8 µm-thick electroplated copper film and 35 µm-thick PI film. The as-received FCCL was cut into several coupons and they were annealed in a convection oven in an air atmosphere at 150, 200, 250 or 300 °C for 15 min. The annealed specimens were immersed in a nitric acid solution for several seconds to remove the surface oxide.

Figure 1 shows the process used for the preparation of the EBSD specimens. The mechanical polishing method was used in this study. Ion etching and FIB are frequently used, but these processes can cause thermal transformation or crystal lattice damage to temperature-sensitive and soft materials. This study employed a simple mechanical polishing process to obtain satisfactory surface quality. The polyimide film was completely removed by immersing the FCCL specimens in a KOH solution at 50 to 60 °C for about 3 h, because the non-conductive film should be removed to help eliminate charging and severe drift problems during long-term EBSD mapping. The copper films were stacked together and then inserted between two dummy copper (phosphor bronze) plates and mounted in a 25 mm diameter brass holder. The mounted specimen was mechanically ground and polished using an Allied Dualprep 3 auto-polisher in conjunction with an AP-4 power head. The specimen was...
ground with silicon carbide papers and then polished with polycrystalline 3 and 1 μm diamond suspensions. Final polishing was done with a 0.05 μm colloidal silica suspension with a pH of 9.8 for 30 min. During polishing, a 13N force was applied to the specimen, and the plate and holder were rotated at 120 rpm. No further treatment, such as electro-polishing, chemical etching, or conductive coating on the surface, was necessary.

#### 2.2 EBSD measurement and analysis

For EBSD mapping, a Tescan Mira II scanning electron microscope incorporating an EDAX-TSL Hikari EBSD detector was used. The magnification of each mapping was 15,000 and the mapping speed was 180 points per second. Each pixel was 30 nm in size and hexagonal in shape. The area size of a single mapping was about $8 \mu m \times 30 \mu m$. A total of 9 or 10 mapping data were gathered for each specimen, giving a total mapping area for each specimen of 2,000–2,500 $\mu m^2$. Number of non-indexed pixels was less than 1% of the total measured pixels and the average confidence index was 0.6 to 0.7.

TSL OIM analysis software version 5.3 was used to analyze the EBSD measurement results. Erroneous pattern indexing was corrected by a clean-up procedure consisting of single iteration grain dilation\(^{19}\) with the parameters of grain tolerance being 5° misorientation and a minimum grain of two pixels. A grain was defined as a single-oriented region divided by high-angle grain boundaries (HAGB). If two neighboring pixels had a misorientation of less than or equal to 15°, they were considered part of the same grain. A grain consisting of less than five pixels was excluded from the grain size calculation. The grain size was defined as the mean intercept length using the linear intercept method. Both vertical and horizontal lines were used and the mean intercept length is defined by

$$d = 1/N$$  \hspace{1cm} (1)

where $d$ is the mean intercept length and $N$ is the number of intersections per unit length of test line with the grains. The average grain size is defined as the geometric mean value of the vertical and horizontal intercept lengths using the following equation.

$$d_{av} = (d_v \times d_h)^{1/2}$$  \hspace{1cm} (2)

where $d_{av}$ is the average grain size, and $d_v$ and $d_h$ are the vertical and horizontal intercept lengths, respectively. A twin boundary was defined as a grain boundary across which the misorientation relationship was a 60° rotation about a (111) crystal axis.

The texture evolution was described by the area fraction of the specific crystallographic direction parallel to the normal direction of the specimen. The calculation of the area fraction was carried out within an angular tolerance of 5°.

#### 3. Results and Discussion

Figure 2 shows the cross-sectional orientation maps of the as-received and annealed copper films. ND is the normal direction and MD is the machine direction of film fabrication. The through-thickness observation of the specimen revealed that the microstructure consisted of very small grains near the interface between the copper film and the polyimide (PI) film and relatively large grains in the remaining area. Figure 3 shows the grain boundary maps of the specimens. The black, grey, and red lines indicate the HAGBs with a boundary misorientation of 15° or larger, low angle grain boundaries (LAGB) with a boundary misorientation of 2° to 15°, and twin boundaries, respectively. The grain boundary structure of the specimen exhibited an HAGB structure with a large amount of twin boundaries. The presence of the LAGBs mainly originated from the substructure inside the grains. Twin boundaries were not as frequently found at the interface as in the remaining area.

Figure 4 shows the grain boundary misorientation histograms of the areas at a distance of 2 μm from the Cu/PI interface toward the Cu surface. The Cu/PI interface regions were excluded from the quantitative analysis, because the grain sizes were too small and the unsolved areas were large. A large fraction of the 60° misoriented boundaries correspond to twin boundaries, and a low fraction of LAGBs indicates that the specimens exhibit an HAGB structure. Except for the LAGBs and twin boundaries, the distribution of the boundary misorientation is close to that for randomly oriented grains, which indicates that the specimens do not have a strong texture. The presence of LAGBs does not seem to be an indication of a well-developed texture, because they were in the substructure inside the grains, as shown in Fig. 3.
The grain structure of metallic films grown by electroplating is influenced by the substrate or seed layer structure. Their epitaxial growth is responsible for the morphology and orientation of the grains near the interface. However, the microstructure in the overall region of the as-received specimen does not resemble that at the interface. This microstructure composed of HAGBs and twin boundaries could be formed during electroplating or room temperature recrystallization right after electroplating (self annealing). The microstructure of the electrodeposits can be changed by increasing the film thickness\textsuperscript{16} and by altering the electroplating conditions.\textsuperscript{17}

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**Fig. 2** Orientation maps of the copper films; (a) as-received, (b) annealed at 150°C, (c) annealed at 200°C, (d) annealed at 250°C, and (e) annealed at 300°C.

**Fig. 3** Grain boundary maps of the copper films; (a) as-received, (b) annealed at 150°C, (c) annealed at 200°C, (d) annealed at 250°C, and (e) annealed at 300°C.
Figure 2 also indicates that the annealing caused grain coarsening. We suggest that the microstructural changes caused by annealing are driven by a normal grain growth mechanism. Recrystallization did not occur even after high temperature annealing at 300°C.

Table 1 shows the area fractions of (111), (100), and (110) ND fiber texture components.

<table>
<thead>
<tr>
<th>Annealing temperature, T/°C</th>
<th>Texture component</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(111)</td>
</tr>
<tr>
<td>Room temperature</td>
<td>0.017</td>
</tr>
<tr>
<td>150</td>
<td>0.024</td>
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<tr>
<td>200</td>
<td>0.025</td>
</tr>
<tr>
<td>250</td>
<td>0.019</td>
</tr>
<tr>
<td>300</td>
<td>0.020</td>
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Figure 5 also shows that the average grain size ($d_{av}$) increased with increasing annealing temperature. As mentioned previously, the increase in the grain size is driven by normal grain growth, and the driving force of grain growth is the reduction of the grain boundary energy. The grain boundary energy can be reduced by reducing the grain boundary length through grain growth. Figure 6 shows the boundary lengths of the LAGBs, total HAGBs, twin boundaries, and general HAGBs as a function of the annealing temperature. A general HAGB was defined as an HAGB excluding twin boundaries, so that a total HAGB is composed of both a general HAGB and twin boundary. General HAGBs rather than total HAGBs are more indicative of high energy grain boundaries, because the interfacial energy of coherent twin boundaries is much lower than that of the average grain boundaries in copper.20) Annealing reduced the lengths of the LAGBs, total HAGBs, and general HAGBs. The twin boundary length was not significantly changed by annealing at 150 or 200°C, but increased when annealing was performed above 200°C (Fig. 6). The increase in the twin boundary length caused by high temperature
annealing is attributed to the generation of annealing twins. During grain growth, annealing twins can be formed in order to reduce the grain boundary energy. The reduction in the number of general HAGBs with a relatively high grain boundary energy is mainly responsible for the reduction of the total HAGB length during high temperature annealing. The modification of the grain boundary characteristics is shown in Fig. 7. The total boundary is composed of the LAGB and the total HAGB. Low temperature annealing at 150 or 200 °C did not appreciably change the fractions of twin boundaries, HAGBs, and LAGBs. Meanwhile, high temperature annealing at 250 and 300 °C increased the fraction of twin boundaries and decreased that of the general HAGBs. After annealing at 300 °C, the twin boundaries accounted for about 60% of the total boundaries. We suggest that annealing causes many of the general HAGBs to be replaced by twin boundaries through grain growth and the formation of annealing twins.

4. Conclusion

The through-thickness EBSD analysis successfully revealed the columnar grain structure of the copper film electroplated on polyimide film. The grain structure of the copper film was characterized by a high angle grain boundary structure with a large fraction of twin boundaries. During annealing, the normal grain growth mechanism is responsible for the increase in the grain size and the decrease in the length of the high angle grain boundaries. During annealing at high temperatures above 250 °C, many of the general high angle grain boundaries were replaced by twin boundaries through grain growth and annealing twinning.

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19) TSL OIM analysis 5.3 manual.