Large-scale Cu nanotwins were electrodeposited in void-free filling within blind microvia using single gelatin as additive in electrolyte. The void-free filling effect was might be caused by a gradient suppressing effect of gelatin along the microvia depth. The gradient distribution of gelatin was resulted from the strong dependence of adsorption on convection force. The adsorbed gelatin might greatly increase the surface tension on the depositing atom plane and then dragged a layer of adatom to a misaligned sites in the lattice, leading to the twinning nucleation.

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Void-Free Filling for Blind Microvia of High Density Interconnect

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Communication—Electrodeposition of Nano-Twinned Cu in Void-Free Filling for Blind Microvia of High Density Interconnect

Nanotwinned copper (nt-Cu) film was firstly synthesized by Lu et al. using pulsed current plating. 1 This nanotwinned structure copper exhibited ultrahigh strength, high elongation, high electrical conductivity and high fatigue cracking resistance. 1–5 In microelectronic field, it was found that the nanotwin-modified Cu grain boundaries could decrease the electromigration-induced atomic diffusion by one magnitude 6 and also reduce the occurrence of the Kirkendall voids. 7,8 The nanotwinned lamellas in different columnar grains were closely paralleled with the substrate plane. Thus, when this deposited layer is used, the convection condition of working electrode was close to that near the microvia entrance in electroplating process. A lower stirring speed of 100 rpm was used to simulate the convection condition at a deeper position of microvia. Meanwhile, the applied current density in galvanostatic measurements was same with that in plating process. After careful polishing and etching, the microstructure of the filled microvia was observed with scanning electron microscopy (SEM, Supra55 Zeiss). The detailed microstructure of nanotwinned grain was characterized with a transmission electron microscopy (TEM, JEOL JEM2100). The twin thickness was measured accurately from above 300 nanotwinned lamellas in TEM images.

Results and Discussion

Fig. 2 showed the filling effects by electroplating using single gelatin as additive with varied concentrations. In the absence of gelatin, there was a significant hollow occurring in the center of the filled Cu, as shown in Fig. 2a. When the gelatin concentration was 50 ppm, a completely void-free filling was achieved. However, further increasing gelatin concentration to 100 ppm, a relatively small seam or void appeared again. It was estimated that the required gelatin concentration to obtain a void-free effect was 40–70 ppm for the present microvia dimension feature. Compared to the approach through the synergistic operation of composite additives, this approach using single additive was easier to operate and control in practical process. In the high magnification images, the filled Cu within microvia contained large columnar grains, and each columnar grain was composed of highly aligned twin lamellas, as shown in Fig. 3a. Although the twin lamellas in some grain were not completely carved out, the number of emerged lamellas appeared a large-scale growth of twinned grain during electrodeposition process. These parallel nanotwinned lamellas predominantly stacked along the grain growth direction. In comparison, the surface deposited layer contained the larger columnar grains, as shown in Fig. 3c. Due to an upward growth direction, the nanotwinned lamellas in different columnar grains were closely paralleled with the substrate plane. Thus, when this deposited layer is patterned to be reaction pad with Sn solder, the high-density twinning boundaries will serve as vacancy sinks during the solid-state reaction and then greatly reduce the formation of Kirkendall voids. 7,16,17 These nanotwinned lamellas were also characterized using TEM observation.

Experimental

The diameter and depth of blind microvia in HDI were about 100 µm and 60 µm respectively. Prior to microvia filling process, the microvia sidewall was metallized by Cu electroless plating and then the Cu film was further thickened by a flash electroplating process, in order to afford a conductive seed layer for the filling process. The basic electrolytes were composed of 200 g/L CuSO4·5H2O, 50 g/L H2SO4, 50 ppm Cl− and various concentrations of gelatin (Molecular weight of 104–105Da). The electrolyte was agitated by a magnet bar at a low stirring speed of 300 rpm. In the plating process, the applied current density was 25 mA/cm2 and the distance of two electrodes at a low stirring speed of 300 rpm. In the plating process, the applied current density was 25 mA/cm2 and the distance of two electrodes was 100 mm. In galvanostatic measurements (GMs), a platinum disk, a platinum foil and a Ag/AgCl electrode were used as the working electrode, counter electrode and reference electrode respectively. The working electrode and counter electrode were placed at the same positions with the HDI sample and anodic Cu plate respectively in the same plating bath. Thus, when a stirring speed of 300 rpm was used, the convection condition of working electrode was close to that near the microvia entrance in electroplating process. A lower stirring speed of 100 rpm was used to simulate the convection condition at a deeper position of microvia. Meanwhile, the applied current density in galvanostatic measurements was same with that in plating process.

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the twin structure was further confirmed through the mirror symmetry relationship of crystallographic planes. Since the (111) plane corresponds to the least surface energy in face-centered cubic (fcc) metal, the Cu atoms are prone to deposit on a (111) plane. Therefore, the Cu nanotwinned lamellas exhibited a strong <111> crystalline along the growth direction, which was consistent with the previously reported results.\textsuperscript{5,7,15,16,17} In TEM image, the measurement result of the lamella thickness along the [110] orientation showed a wide distribution ranging from several nanometers to about 100 nm, as shown in Fig. 3f. The average thickness was calculated to be about 25 nm, which slightly larger than those prepared by pulsed electroplating.\textsuperscript{1,2,14}

From the GMs plots, as shown in Fig. 4, the electrolytes with gelatin exhibited a much more negative potential than that without gelatin, which indicated that the gelatin had a strong suppressing effect. Without gelatin, the potential at 300 rpm was obviously more positive than that at 100 rpm, which demonstrated that the deposition rate at the entrance was much higher than that at the deeper position. Thus, a premature closure of entrance would leave a void

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**Figure 1.** Illustration of high density interconnect through Cu filled blind-microvias.

**Figure 2.** Cross-sectional views of the filled Cu within microvias after electroplating using gelatin with various concentrations: (a) 0 ppm, (b) 50 ppm, (c) 100 ppm.

**Figure 3.** Microstructure of nanotwinned Cu: (a) filled Cu within blind microvia, (b) deposited Cu layer on surface, (c) (d) magnified images of marked zones in (a) and (b) images respectively, (e) TEM image with the corresponding [110] Cu diffraction pattern, (f) distribution of the twin lamella thicknesses.
within the filled Cu. For 50 ppm gelatin, it was interestingly noted that the potential at 300 rpm was more negative than that at 100 rpm, which implied that the deposition rate at the entrance was lower than that at the deeper position. A “gradient suppressing”, i.e., the weaker suppressing effect at the deeper location of microvia, was proposed to explain this filling mode within the microvia. The “gradient suppressing” was generally contributed from the gradient distribution of suppressor adsorption on the convection force, as illustrated by the inserted image in Fig. 4. The gradient distribution of a suppressor could lead to the greater deposition rate at the deeper location, forming a “V” shaped filling profile. This “V” shaped profile usually corresponded to a void-free filling effect for blind microvia. When the gelatin was increased to an excessive concentration of 100 ppm, such a gradient distribution is difficult to be formed and then led to an approximately conformal filling mode. This conformal mode was reflected by a similar potential between 300 rpm and 100 rpm in chronopotentiometry curve. The conformal deposition may eventually leave a seam in the middle of filled Cu.\(^{13}\)

During pulse electrodeposition, the formation of nanotwins was associated with relaxation of the stress induced during deposition under high current density. \(^{2,3}\) In DC electrodeposition, the nanotwins could be formed using gelatin as additive under high agitation speed and current density. \(^{15,16}\) We believed that these factors facilitated the generation of high stress by lattice distortion and then the stress was relaxed by formation of the twins. The possible mechanism is that the gelatin greatly increase the surface tension on the depositing plane. The surface tension can drag a layer of adatoms to misarranged sites in the lattice, leading to the formation of twin or stacking fault. \(^{19}\) It is similar to the stress induced twinning nucleation in high speed deformation of the metal with low stacking fault energy. When the PEG as a surfactant was added into the electrolyte to decrease surface tension of depositing atom plane, the formation of nanotwins was seldom observed experimentally, which supported this assumed mechanism of twinning formation using single gelatin.

Conclusions

A void-free Cu filling for blind microvia of HDI was obtained and simultaneously large-scale nanotwinned grains were fabricated in the filled structure by electroplating using single gelatin as additive. The large columnar grains were composed of high-density nanotwinned lamellas with a strong <111> crystalline along the growth direction. The void-free filling was formed by a gradient suppressing effect due to a strong dependence of gelatin adsorption on the convection force. The gelatin adsorption might greatly increase the surface tension on the depositing atom plane and this surface tension led to the twinning nucleation.

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Figure 4. Galvanostatic measurements (GMs) of Cu electrolytes with gelatin additive at varied concentrations and varied stirring speeds, and an inserted schematic image of “gradient suppressing” effect.