1. Introduction

Recently, the performance and the density of semiconductor devices have been improved remarkably. For ensuring the improved performance and density, a large number of I/O terminals and a high wiring density are required for the package substrate. The ITRS roadmap for microprocessor packages estimates that the width of a copper line will decrease to less than 10 μm in 2014.[1]

Since the adhesion strength between copper and epoxy resin, which is used as an insulation layer, is very low, the surface of the epoxy resin is roughened to approximately 5 μm by using an etching solution such as permanganate in order to improve the adhesion strength. However, while making a fine pattern that is narrower than 10 μm, the rough surface may cause a short circuit. This is because some copper residue between the wirings remains after etching because of the diffusion of the reflection during the exposure process, where the diffusion depth depends on the roughness.

Recently, some technologies that achieved the chemical adhesion strength between electroless copper and the insulation layer, e.g., by introducing hydroxyl groups and a coupling agent on the insulation layer,[2] by introducing other special coupling agents for the epoxy resin,[3–4] or by modifying the surface of the insulation layer by UV irradiation,[5–6] have been reported.

On the other hand, a fine-pitch wiring technology has been developed by introducing the chromium compound adhesion promoter layer on the surface of smooth epoxy resin.[7] In this reference, a chromium compound was introduced by transferring the adhesion layer from a copper foil to the smooth epoxy resin.

However, when this technique was applied to the manufacturing of multi-layer printed circuit boards, the conventional via formation process was found to damage the adhesion layer and roughen the epoxy resin. In order to make vias in the insulation layer for the build-up layer, the printed circuit board is exposed to the CO₂ laser. After the via formation, some residue called smear is removed by permanganate. However, the permanganate solution removes not only the smear but also the adhesion layer, leading to the roughness of the epoxy.

In this study, a via formation process that does not damage the adhesion layer is investigated. First, the adhesion layer is transferred onto the insulation layer, followed by the DFR lamination to protect the adhesion layer from
following process. Then, the effect of the plasma condition on the smear removal rate and that of the type of DFR remover on the adhesion layer are investigated.

2. Experimental Procedure

2.1 Via formation process

The outline of the via formation process is shown in Fig. 1. First, a copper foil whose one side was coated with the chromium compound adhesion layer was laminated on the epoxy resin. The chromium compound was coated by chromate treatment. The copper foil was very smooth as its roughness was 1.2 \( \mu \text{m} \), as shown in Fig. 2.

Then, the copper foil was removed by the copper chloride etchant in order to leave the adhesion layer on the epoxy resin.[7] Next, the adhesion layer was covered with a protective layer. Then, the \( \text{CO}_2 \) laser was irradiated on the protective layer to form via holes in the epoxy resin. The smear, which was the residual resin and was formed during the laser abrasion process, was removed by using a plasma treatment on the remains of the protective layer. Finally, the protective layer was removed from the adhesion layer. After these processes, 0.3 \( \mu \text{m} \) thick electroless copper seed layer was deposited on the adhesion layer.

2.2 Insulating layer

An insulating layer composed of epoxy resin and 35-wt% silica filler (diameter: 0.3–1.0 \( \mu \text{m} \)) was used. The thickness of the insulating layer was 40 \( \mu \text{m} \). After the lamination of the epoxy resin and the copper foil, the insulating layer was cured at 180°C for 1 h.

2.3 Selection of protection film

A 25 \( \mu \text{m} \) thick DFR layer was selected to protect from the damage caused by the following processes because of laser processibility, removability, and thickness control, as shown in Table 1. The Cu foil could be used as the protective layer; however, the via diameter was larger than that without the protective layer because of the laser power.[8] A UV laser could be used for obtaining a small via, but the laser equipment would have to be replaced in a manufacturing factory. In this paper, 40 \( \mu \text{m} \) thick insulation layer, our target was to make a small via hole of 50 \( \mu \text{m} \) by using \( \text{CO}_2 \) laser.

2.4 Peel strength test

A 35 \( \mu \text{m} \) thick copper layer was electroplated on the electroless copper for the peel strength test. In the test specimens, a number of 1 cm wide cuts were made through the Cu layer. The peel strengths were measured using a peel strength tester equipped with a digital force gauge. The number of measurements was more than three for each specimen and took an average. Considering the total thermal impact of the four-layer double-side build-up printed circuit board fabrication process, we cured the specimens four more times at 180°C for 1 h and the reflow process was carried out five times at 260°C for 1 min.

3. Results and Discussion

3.1 Peel strength

Figure 3 shows the peel strength of the Cu layer on the adhesion layer and that on the conventional desmear
rough surface. High peel strength of 1 kN/m was obtained for the Cu layer on the adhesion layer. It was higher than that of the conventional desmear rough surface. The conventional desmear process had 3-step, alkaline solvent for pre-treatment, permanganese for etching and acid solution for neutralize and remove the manganese residues. Even after the reflow process, which was followed by the curing process, the obtained peel strength was as high as 0.8 kN/m, which was still higher than that obtained in the case of the desmear surface. The 10-point average roughness of Rz for the transfer method was approximately 0.7 μm, which was very small as compared to the desmear surface roughness of 3 μm. As shown in Fig. 3, very high peel strength with a smooth epoxy surface is obtained by transferring the adhesion layer. The surface of peeling copper shows the residue of the resin, so the fracture mode is destroying of the resin.

Figure 4 shows the SEM micrograph of a 10 μm line and space on epoxy resin surface by using the transfer method. No delamination was observed.

### 3.2 Adhesion mechanism

In order to clarify the mechanism of adhesion strength improvement, x-ray photoelectron spectroscopy (XPS) was carried out on the surface of epoxy resin after the transfer of the adhesion layer and etched the copper foil by the copper chloride as an etchant (Fig. 5). The peak at 574 and 583 eV, which indicate Cr 2p, were observed. Further, the energy peaks from the carbonyl group and the metal-oxide were observed using XPS narrow scan spectra as shown in Fig. 6. The chromium compound was removed by using a mixture of sulfuric acid and hydrogen peroxide as an etchant, the peel strength was dropped to 0.4 kN/m after the reflow.[7] Therefore, we believe that the chromate compound such as chromium oxide or hydroxide bridges the electroless copper and the epoxy resin to improve the peel strength.

It is also believed that the chromium compound does not remain between the wiring because there is no chromium compound after etching by using a mixture of sulfuric acid and hydrogen peroxide.[7] Figure 7 shows the adhesion mechanism between the epoxy resin and the electroless copper. Chromium compounds make strong chemical bonds with Pd and resin surfaces, leading to the strong peel strength between Cu and the epoxy resin.
3.3 Via formation and via structure

After the etching of the copper foil, DFR was laminated on the adhesion layer. DFR consists of the acrylic resin. Then, CO₂ laser was irradiated over the DFR layer through the epoxy resin; the structure of the sample is shown in Fig. 8. The laser power was 1.63 mJ, 5 shot for 40 μm thick epoxy resin and 25 μm thick DFR.

Figure 9 shows the SEM micrographs of the via hole. The top view reveals that the shape of the via with DFR shown in Fig. 9(a) is similar to that of the conventional one as shown in Fig. 9(c). The via diameter with DFR is smaller than the diameter of the conventional via because of the total thickness. On the other hand, the cross-sectional view as shown in Fig. 9(b) reveals that the tapered shape of the newly formed via is similar to that of a conventional one.

3.4 Plasma desmear condition

After the laser shot, the residue of the mixture of the resin and some filler, the so-called smear, remains on the bottom of the via hole, as shown in Fig. 10(a). Figure 10(b) shows the bottom of the via hole after a plasma treatment using an O₂/CF₄ mixture gas. It is seen that the smear is removed by 10 min of the plasma treatment when the plasma power is 6 kW at 250 mTorr. However, some residue is remained after a plasma treatment using O₂ gas only or after 5 min of the earlier plasma treatment, as shown in Figs. 10(c) and (d), respectively. The surface of the DFR is also etched by using the plasma of the O₂/CF₄ mixture gas. Under this condition, the etching rate of the epoxy resin and the DFR is 0.4 μm/min and 1.5 μm/min, respectively, as shown in Fig. 11. The etching rate of epoxy resin with filler is almost 0, so the CF₄ gas accelerate the etching rate to remove the epoxy resin with filler.

15 μm of 25 μm thick DFR is etched during the smear removal, and 10 μm of the DFR remains; therefore, there is no damage on the surface of the adhesion layer on the epoxy resin.

3.5 Removal of DFR

The removability of some removers is listed in Table 2. After the plasma treatment to remove the smear, it was found that DFR was difficult to remove by conventional sodium hydroxide (NaOH); it took 10 times longer time than in the case in which the plasma treatment was not carried out because the temperature of the DFR surface...
reached a value higher than 90°C during the plasma treatment, which led to the reaction the DFR with epoxy resin. So the DFR was hard to remove by conventional sodium hydroxide and dipping long time in sodium hydroxide led to damage to epoxy surface. On the other hand, an amine-type remover can remove DFR in 90 s because it can easily permeate into DFR.

3.6 Adhesion strength after removal of DFR

Figure 12 shows the peel strength of the Cu layer after the DFR removal when two types of removers are used. When the amine-type remover is used as the DFR remover, a high peel strength of 0.9 kN/m is obtained as prepared and 0.7 kN/m is obtained after reflow, which is almost the same as that for a conventional rough surface. On the other hand, when sodium hydroxide is used as the DFR remover, the peel strength of 0.7 kN/m is measured as prepared; the peel strength decreases to 0.4 kN/m after the reflow. 0.8 μm of the surface roughness fell to 0.6 μm after sodium hydroxide treatment, there may be some damage to the surface of the epoxy resin due to sodium hydroxide. On the other hand, the roughness was 0.75 μm after amine-type remover treatment, it was almost same as without via formation process. Therefore, we can conclude that the amine-type remover is good for removability and peel strength. The fracture mode was the destroying of the resin for without via formation process, the interfacial peeling for with via formation process.

3.7 Adhesion layer after removal of DFR

Figure 13 shows the XPS spectrum of the surface of the epoxy resin after the DFR removal by an amine-type remover. The energy peaks from the chromium compound adhesion layer are still observed, which indicates the existence of the adhesion layer even after the via formation process. The remaining adhesion layer maintains the high peel strength.

4. Conclusion

A new via formation process that helped achieves a high peel strength and a smooth surface was developed, and the mechanism of the high peel strength was clarified. The transfer of the adhesion layer led to a high peel strength of 1 kN/m with a smooth epoxy surface, which was as high as that of the rough surface obtained by the conventional desmear process. In order to protect the adhesion layer, the DFR was laminated on the adhesion layer, and then, CO₂ laser was exposed over the DFR. After the laser shot, the smear was found to be removed effectively by the plasma treatment with an O₂/CF₄ mixture gas. Finally, DFR was removed by an amine-type remover, while some of the adhesion layer remained on the epoxy resin, leading to a high peel strength of 0.9 kN/m.

References


Shinya Sasaki received his B.S. and Ph.D. degrees in Organic Chemistry from Tohoku University, Sendai, Japan, in 1994 and 1999, respectively. He joined Fujitsu Laboratories Ltd. in 1999. Since then, he has been engaged in the research and development of advanced materials for microelectronics.

Motoaki Tani received his B.S. and M.S. degrees in Engineering Science from Osaka University, Osaka, Japan, in 1985 and 1987, respectively. He joined Fujitsu Laboratories Ltd. in 1987. Since then, he has been engaged in the research and development of advanced materials for microelectronics. He received his Ph. D. degree from Osaka University, Osaka, Japan, in 2013. He is currently the Director of Electronics Packaging Laboratory.