Effects of Polyethylene glycol derivative for Electro Copper Plating.

Kazuki Yamaguchi, Masaharu Sugimoto, Hiroaki Kouzai, Hiroki Nagashima, Kimiko Oyamada, Hideo Honma
Department of Applied Material and Life Science, College of Engineering, Kanto Gakuin University, 1-50-1 Mutsuura-higashi, Kanazawa-ku, 235-8501, Japan
Kanto Gakuin University Surface Engineering Research Institute
4-4-1 Ikeda-cho, Yokosuka-shi, Kanagawa 239-0806, Japan

1, Introduction

Recently, miniaturizations of printed circuit boards (PCBs) have become essential with the downsizing of electronic devices. But conventional multi-layered PCBs have a limitation to higher packaging densities. Build-up process, the layer-to-layer connection with via-hole for inter connection, has been adopted as a new PCB manufacturing process. In this technology, via-holes are used to connect each conductive layer. Via-holes are filled with a resin after the interlayer connection by copper electroplating. However, the voids are often generated in via-holes with the shrinkage of the holes. The void becomes the problem of connection reliability. As the conductor patterns become finer, a filling of via-holes by copper plating has become an effective method. The method has been called via-filling.

Via-filling is controlled by the various organic compounds called additives, and the proper combination and concentration of additives are effective for copper deposition.

In this study, we synthesized Polyethylene glycol (PEG) derivative as carrier, and examine the influence of end chain group to via-filling.

2, Experimental

2-1, Synthesis of Diphenoxy Polyethylene glycol (PEG-Ph)

PEG-Ph was synthesized by following method. PEG-Cl (5 mmol) (*Mw*=4,000), phenol (12 mmol), K_2CO_3 (12 mmol) and DMF (*N*,*N*-dimethylformamide) (30 cm^3) were refluxed 48 hour in the N_2 atmosphere. The hot reaction mixture was filtered off, and then the liquid was placed under the room temperature. The reaction mixture was put in to a cold diethylether (500 cm^3). The precipitate was collected by filtration. PEG-Ph was purified by the following procedure. PEG-Ph was dissolved with dichloromethane and filtratered. The solution was placed into cold diethylether and the precipitate was collected by filtration. Obtained PEG-Ph after 3 times precipitation operation was dried under resuced pressure.

2-2, Via-filling

The resin testsample comprsing the vias of in 60~130 μ m width and 60 μ m in height were used as the evaluation of via-filling. The compositions and operating conditions of plating bath are shown in **Table 1**. PEG, PEG-Ph, bis (3-sulfopropyl) disulfide disodium (SPS) and Janus Green B (JGB) were used as additives. The result of via-filling, Cu-layer was evaluated by calculating filling-ratio **(Fig. 1.)**.

3, Results and discussion

3-1, Synthesis of PEG-Ph

The product was characterized by FT-IR (ATR method), ^{1}H-NMR and ^{13}C-NMR. The yield of PEG-Ph was 40% that is gray powder. The synthesis of PEG-Ph was confirmed by the analysis : Each structure was identical with spectra of PEG-Ph.

3-2, Influence of PEG-Ph on via-filling

As shown in **Table 2**, complete void-free features on the vias and smooth copper deposits were not obtained from PEG bath (Cl-ion free). However, good filling ratio was obtained at PEG-Ph (Cl-ion free). From these results, PEG-Ph has a different suppress mechanism for metal adsorption. Accordingly, amount of adsorption to electrode surface of each PEGs were measured by Electro Quartz Crystal Microbalance (EQCM) method. As a results of EQCM measurements, the value of PEG changed 526.89 $\times 10^{-8}$ g (with Cl-ion) to 258.52 $\times 10^{-8}$ g (Cl-ion free), but PEG-Ph changed 70.89 $\times 10^{-8}$ g (with Cl-ion) to 44.27 $\times 10^{-8}$ g (Cl-ion free). From there results, PEG-Ph has a different suppress mechanism from PEG.

4, Conclusion

Good filling ratio was obtained from PEG-Ph (Cl-ion free) bath. By EQCM, there is possibility that PEG-Ph was not use Cl-ion for adsorption in metal. PEG-Ph showed the suppress action that differs with PEG.

5, Acknowledgment

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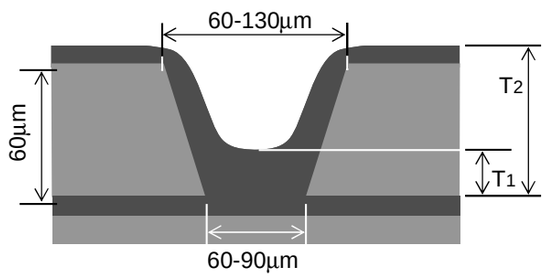

Filling Ratio(F.R.)
$= T_1 / T_2 \times 100$

Fig. 1. Schematic representation of the test sample.

Table 1. Bath compositions and operating conditions for electro copper plating

High throwing bath	
$CuSO_4 \cdot 5H_2O$	65 g/dm^3
H_2SO_4	200 g/dm^3
Cl^-	0 or 0.05 g/dm^3
Current Density	1 A/dm^2
Agitation	mechanical
Plating Time	114 min.

Table 2. Results of Via-filling (Filling ratio)

	130μm		80μm		60μm	
Cl^-	○	×	○	×	○	×
PEG	69 %	39 %	74 %	36 %	69 %	76 %
PEG-Ph	50 %	209 %	36 %	95 %	34 %	void