

# Synthesis and Practicability of Novel Additives for Copper Electroplating with Semiconductor Packaging

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**ABSTRACT:** Connection reliability between Large Scale Integrated circuit (LSI) and electronic devices is increasingly important with the miniaturization of electronic devices. For the formation of fine conductors on wiring in electronic devices, copper electroplating is generally applied and is controlled with various organic additives. In this study, for the purpose of developing additives capable of working on a finer conductive copper circuit, we focused our attention on the synthesis of organic additives with inhibition action for the plating. Generally, poly(ethylene glycol) (PEG) was used as an inhibitor. We synthesized the PEG derivatives,

which were  $\alpha$ -(2-chloroethyl)- $\omega$ -chloropoly(oxyethylene) (PEG-Cl) and  $\alpha$ -(2-sulfoethyl)- $\omega$ -sulfopoly(oxyethylene)disodium, and evaluated them for their Via-filling properties. Good filling properties were achieved by the addition of these synthesized materials to a normal copper-plating bath. Furthermore, with PEG-Cl, good filling properties were achieved without chlorine ions, which were usually added to the bath. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 837–840, 2005

**Key words:** oligomers; polyethers; water-soluble polymers

## INTRODUCTION

As a result of the miniaturization and performance enhancement of electronic devices, such as cellular phones and personal computers, in recent years, the densification and multilayering of printed wiring boards are required. Conventionally, through-holes are used for the interlayer connections in multilayer printed wiring boards. However, a through-hole suited to the finer scale of printed wiring boards is becoming difficult to produce. Accordingly, a construction method in which Vias are used for interlayer connections is attracting attention. This construction method involves laminating conductive layers and insulating layers alternately and performing interlayer connections with Vias. Generally, in the case of lamination, the interior of a Via is made electroconductive by electroless copper plating, which is followed by conformal copper electroplating, and the Via is filled up with an insulating resin or a conductive paste.

However, in this process, a void or seam inside the Via or a dimple in an upper portion often occurs, and this results in problems such as a lack of connection reliability and a delay of signal transmission. As a technique for solving this problem, Via filling, in which the whole Via is filled with copper by electroplating, has attracted attention. Furthermore, an attempt has recently been made to make Vias subjected to Via filling through respective layers constituting a stack Via structure.<sup>1</sup> The achievement of that structure is expected to lead to significant densification of wiring and high-speed propagation.

From this perspective, many studies have recently been reported on Via filling with copper plating,<sup>2–6</sup> and the realization of Via filling with electroless plating or a periodical reverse electrolytic method has been reported.<sup>7–9</sup> In addition, Via filling with additives, with control over the kinds and concentrations of the additives, has been accomplished.<sup>10</sup>

Nowadays, various additives are used in Via filling. Additives may be divided into three types according to their effects: promoters (brighteners), inhibitors (carriers), and smoothing agents (levelers). A disulfide compound such as bis(3-sulfopropyl)disulfide disodium (SPS) is used as a brightener and promotes the deposition of copper. A polyether such as poly(ethylene glycol) (PEG) is used as a carrier and inhibits the deposition of copper. In the presence of chlorine ions, PEG strongly adsorbs onto the surface of copper and

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inhibits the deposition of copper.<sup>11,12</sup> Janus Green B (JGB) is used as a leveler and adjusts deposition during plating; this results in a smooth copper surface. The addition of a mixture of additives allows good filling without voids or seams. However, in the future, a Via-filling technique for various Via diameters or high aspect ratios will be required because of the densification of printed wiring boards.

Accordingly, we attempted to develop additives with performances higher than those of conventional additives. Specifically, two PEG 4000 derivatives,  $\alpha$ -(2-chloroethyl)- $\omega$ -chloropoly(oxyethylene) (PEG-Cl) and  $\alpha$ -(2-sulfoethyl)- $\omega$ -sulfopoly(oxyethylene)disodium (PEG-SO<sub>3</sub>Na), to which chlorine and sodium sulfonate, respectively, were added, were synthesized. The difference in their effects was examined, their Via-filling ability was evaluated.

## EXPERIMENTAL

### Materials

SPS, synthesized from 3-mercapto-1-propanoic sulfonic acid sodium salt, was purchased from Tokyo Kasei Kogyo Co., Ltd. (Japan) PEG was purchased from Kanto Kagaku Co., Ltd. (Japan) and recrystallized in isopropyl alcohol before use. Other solvents and reagents were used as received.

### Synthesis of the additives

#### Synthesis of PEG-Cl<sup>12-14</sup>

Thionyl chloride (5 cm<sup>3</sup>) was added dropwise to 2.0 g (0.5 mmol) of a PEG powder in an ice-cooled water bath. After the addition, the resultant mixture was gradually heated and subjected to heating and stirring at 60°C overnight. The obtained reaction solution was mixed in 50 cm<sup>3</sup> of diethyl ether, which corresponded to about 10 times the amount of the solution, and the mixture was isolated. After the precipitate was suction-filtered, it was dried under reduced pressure and was recrystallized in isopropyl alcohol, A white solid (1.96 g) was obtained in a yield of 98%; the melting point was 58.3°C.

#### Synthesis of PEG-SO<sub>3</sub>Na<sup>14</sup>

PEG-Cl (2.0 g, 0.5 mmol), 0.4 g (3.1 mmol) of Na<sub>2</sub>SO<sub>3</sub>, 6 cm<sup>3</sup> of water, and 2 cm<sup>3</sup> of ethanol were mixed and refluxed for 48 h. After the reaction, 0.04 g of activated carbon was added, the mixture was stirred for 2 h, and then the activated carbon was removed. The solvent was removed from the obtained filtrate with an evaporator. Methylene chloride (10 cm<sup>3</sup>) was added to the product, and insoluble matter was removed. The filtrate was mixed in an amount of diethyl ether about 10 times that of the filtrate, and the mixture was isolated.

After the precipitate was filtered, it was dried and recrystallized in isopropyl alcohol; 1.2 g of a white powder (60% yield) was obtained. The melting point was 57.6°C.

### Characterization of the additives

IR spectra were measured with a Spectrum One spectrometer (PerkinElmer Co., Ltd., Japan). NMR spectra in solution were recorded on a Varian Mercury 400 spectrometer (Vaian Technologies Co., Ltd., Japan). A Hull cell test was conducted on a Yamamoto-MS Co., Ltd. (Japan), apparatus. An electrochemical analysis was conducted according to cyclic voltammetry (CV) with a Hokuto Denko HZ-3000 (Hokuto Denko Co., Ltd., Japan) for electrochemical measurements.

## RESULTS AND DISCUSSION

### Synthesis of the additives

#### Synthesis of PEG-Cl

In the IR measurements of the product, stretching vibrations of C—H of a methylene group at 2883 cm<sup>-1</sup>, antisymmetric stretching vibrations of C—O—C of aliphatic ether at 1098 cm<sup>-1</sup>, and stretching vibrations of C—Cl at 665 cm<sup>-1</sup> were assigned. In the <sup>1</sup>H-NMR measurements, a methylene proton adjacent to an oxygen atom at 3.66 ppm and a methylene proton adjacent to a chlorine atom at 3.75 ppm were assigned. In the <sup>13</sup>C-NMR measurements, a methylene carbon atom adjacent to a chlorine atom at 43.0 ppm, a methylene carbon atom adjacent to an oxygen atom at 70.6 ppm, and a methylene carbon atom at the  $\beta$  position of a chlorine atom at 71.5 ppm were assigned [Fig. 1(a)]. On the basis of these results, we concluded that PEG-Cl was obtained.

#### Synthesis of PEG-SO<sub>3</sub>Na

In the IR measurements of the product, stretching vibrations of C—H of a methylene group at 2981 and 2884 cm<sup>-1</sup> and antisymmetric stretching vibrations of C—O—C of aliphatic ether at 1106 cm<sup>-1</sup> were confirmed. In the <sup>1</sup>H-NMR measurements, a methylene proton adjacent to a sulfonic acid group at 3.13 ppm, a methylene proton adjacent to an oxygen atom in the range of 3.60–3.73 ppm, and a methylene proton at the 13-position of a sulfonic acid group at 3.92 ppm were confirmed. In the <sup>13</sup>C-NMR measurements, a methylene carbon atom adjacent to a sulfonic acid group at 50.8 ppm, a methylene carbon atom at the 13-position of a sulfonic acid group at 67.6 ppm, and a methylene carbon atom at the a position of an oxygen atom in the range of 69.4–70.7 ppm were assigned [Fig. 1(b)]. On the basis of these results, we concluded that PEG-SO<sub>3</sub>Na was obtained.

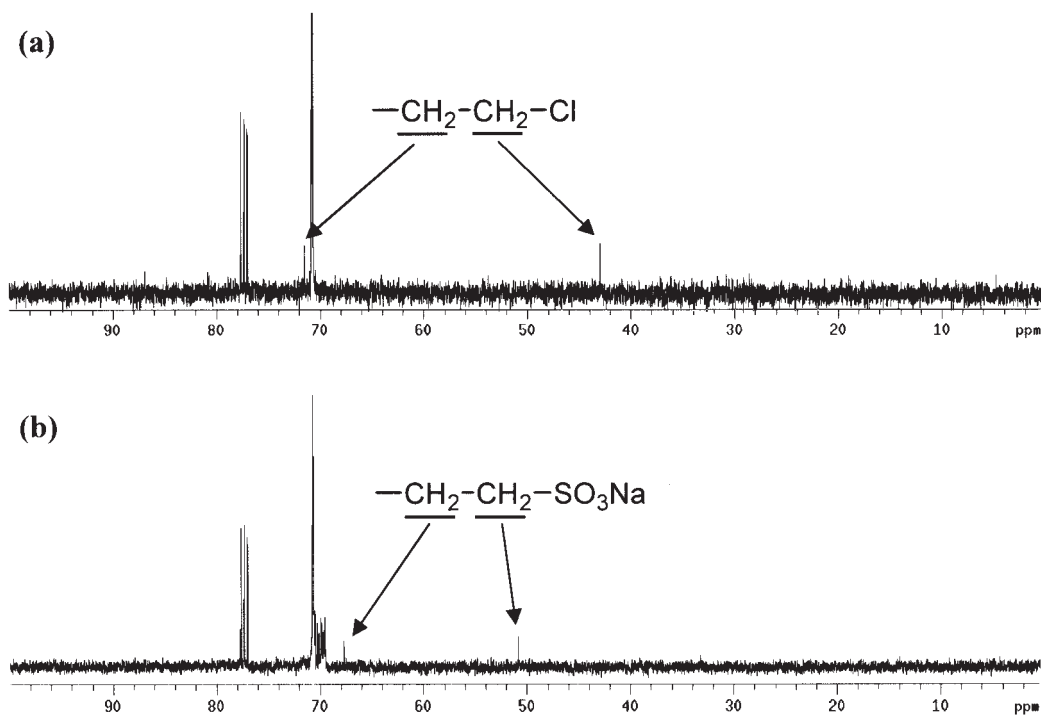


Figure 1  $^{13}\text{C}$ -NMR spectra of (a) PEG-Cl and (b) PEG- $\text{SO}_3\text{Na}$  in  $\text{CDCl}_3$ .

### Evaluation by a Hull cell test

The differences between the synthesized additives were examined with a Hull cell test, in which each synthesized additive was added to a bath, and the practicality of Via filling was also examined. The plating bath used for the experiments was a general copper-plating bath containing  $200\text{ g dm}^{-3}$  copper sulfate and  $50\text{ g dm}^{-3}$  sulfuric acid. The bath temperature was  $25^\circ\text{C}$ , the current density was  $2\text{ A dm}^{-2}$ , and the plating time was 10 min.

For the evaluation of the carrier, PEG-Cl and PEG- $\text{SO}_3\text{Na}$  were used. SPS ( $1.0 \times 10^{-4}\text{ mol dm}^{-3}$ ), a synthesized carrier ( $2.5 \times 10^{-6}\text{ mol dm}^{-3}$ ), and hydrochloric acid ( $\text{HCl}$ ;  $4.0 \times 10^{-3}\text{ mol dm}^{-3}$ ) were added to the bath for the Hull cell test. Both PEG-Cl and PEG- $\text{SO}_3\text{Na}$  showed wide brightening ranges of 0.8–12.0 and 0.2–12.0  $\text{A dm}^{-2}$ , respectively. Furthermore, both synthesized PEG-Cl and PEG- $\text{SO}_3\text{Na}$  created a wide brightening range equivalent to that of PEG, from a high current to a low current. PEG- $\text{SO}_3\text{Na}$  had wider range and excellent brightness.

### Evaluation by electrochemical measurements

The depolarizing and polarizing action of an additive was measured via electrochemical measurements (CV method) during the addition of a synthesized additive to a bath. Plating deposition is apt to be promoted when depolarization action is strong, whereas plating is apt to be inhibited when polarization action is

strong. The composition of the general bath used for the measurements was  $200\text{ g dm}^{-3}$  copper sulfate and  $50\text{ g dm}^{-3}$  sulfuric acid.

The measurements of PEG-Cl and PEG- $\text{SO}_3\text{Na}$  revealed that both exhibited a polarization effect similar to that of PEG, which is generally used for copper electroplating. The strength of the effect was in the following order: PEG- $\text{SO}_3\text{Na}$  > PEG > PEG-Cl. Consequently, it was thought that PEG-Cl and PEG- $\text{SO}_3\text{Na}$  also worked as carriers.

### Evaluation by Via filling

Through the addition of a synthesized additive to the bath and Via filling, we determined whether it was actually possible to carry out filling. The composition of the bath used for Via filling was  $65\text{ g dm}^{-3}$  copper sulfide and  $200\text{ g dm}^{-3}$  sulfuric acid (a common composition). The bath temperature was  $25^\circ\text{C}$ , the current

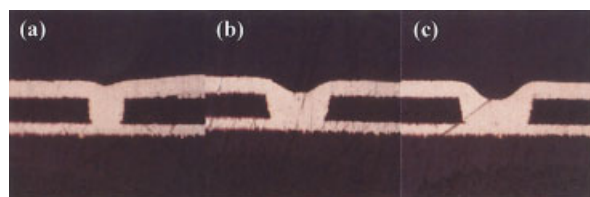
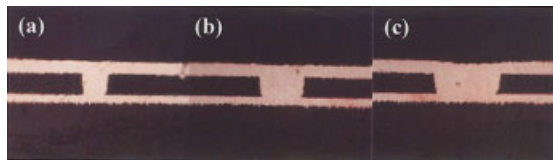


Figure 2 Results of Via filling (addition of SPS, PEG-Cl, JGB, and HCl). The diameters were (a) 60, (b) 80, and (c) 130  $\mu\text{m}$ .



**Figure 3** Results of Via filling (addition of SPS, PEG-SO<sub>3</sub>Na, JGB, and HCl). The diameters were (a) 60, (b) 80, and (c) 130  $\mu\text{m}$ .

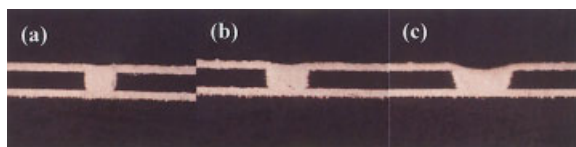
density was  $1 \text{ A dm}^{-2}$ , and the plating time was 114 min. The diameter of the filled Via was 130, 80, or 60  $\mu\text{m}$ .

A brightener evaluation was performed for SPS, and it was confirmed to create a wide brightening region in the Hull cell test and to exhibit a high depolarizing effect in the electrochemical measurements. The effect of SPS has already been reported. SPS ( $1.0 \times 10^{-4} \text{ mol cm}^{-3}$ ), PEG ( $2.5 \times 10^{-6} \text{ mol dm}^{-3}$ ), JGB ( $2.0 \times 10^{-5} \text{ mol dm}^{-3}$ ), and HCl ( $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) were the additives added to the bath to conduct Via filling. As a result, good filling without voids and seams was achieved. Consequently, it was confirmed that synthesized SPS had an effect as a brightener.

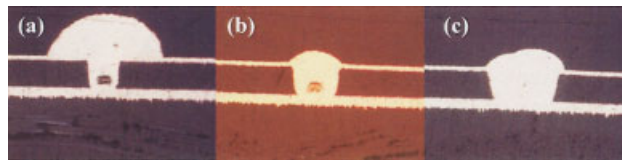
PEG-Cl and PEG-SO<sub>3</sub>Na were subjected to carrier evaluation. SPS ( $1.0 \times 10^{-4} \text{ mol cm}^{-3}$ ), synthesized PEG-Cl or PEG-SO<sub>3</sub>Na ( $2.5 \times 10^{-6} \text{ mol dm}^{-3}$ ), JGB ( $2.0 \times 10^{-5} \text{ mol dm}^{-3}$ ), and HCl ( $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) were the additives added to the bath to conduct Via filling. Both carriers exhibited good filling without any voids or seams in the vias (Figs. 2 and 3).

In addition, Via filling was conducted with  $1.0 \times 10^{-4} \text{ mol cm}^{-3}$  SPS,  $2.5 \times 10^{-6} \text{ mol dm}^{-3}$  PEG-Cl, and  $2.0 \times 10^{-5} \text{ mol dm}^{-3}$  JGB (without HCl). Good filling was achieved with PEG-Cl with the bath without the chlorine ions (Fig. 4). PEG-Cl showed almost the same inhibition as PEG and HCl.

Furthermore, Via filling was conducted with  $2.5 \times 10^{-6} \text{ mol dm}^{-3}$  PEG-SO<sub>3</sub>Na,  $2.0 \times 10^{-5} \text{ mol dm}^{-3}$  JGB, and  $4.0 \times 10^{-3} \text{ mol dm}^{-3}$  HCl, and filling was possible in a Via 130  $\mu\text{m}$  in diameter (Fig. 5). However, the state of plating was crude, and microvoids were generated. On the other hand, the flat part of the copper film became thinner, and this indicated strong adsorption of PEG-SO<sub>3</sub>Na onto the surface of copper that inhibited the deposition of copper. Consequently,



**Figure 4** Results of Via filling (addition of SPS, PEG-Cl, and JGB). The diameters were (a) 60, (b) 80, and (c) 130  $\mu\text{m}$ .



**Figure 5** Results of Via filling (addition of PEG-SO<sub>3</sub>Na, JGB, and HCl). The diameters were (a) 60, (b) 80, and (c) 130  $\mu\text{m}$ .

the copper deposition to the Via was promoted, and the deposition became remarkable, like a bump.

## CONCLUSIONS

In this study, PEG-Cl and PEG-SO<sub>3</sub>Na, derivatives of PEG (which is currently used as a carrier), were synthesized.

In the presence of chlorine ions, PEG-Cl exhibits an effect similar to that of PEG, which is usually used, and this allows good Via filling without chlorine ions, which are conventionally required. Consequently, adjusting the concentration of chlorine ions, which is difficult, becomes unnecessary, and this makes the maintenance of the bath easy. Furthermore, as a result of fewer kinds of additives, the benefit of easy controllability of the plating path can be expected.

PEG-SO<sub>3</sub>Na has a plating inhibition effect that is slightly higher than that of PEG. Via filling (130  $\mu\text{m}$  in diameter) can be achieved with PEG-SO<sub>3</sub>Na without SPS. Via filling is possible with PEG derivatives without SPS and HCl.

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