Electrochemical Analysis of Aged Copper Plating Bath in Wafer Level Packaging (Part 1)

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Abstract

Copper electroplating processes are widely used in semiconductor manufacturing, particularly during the packaging stage [1]. Copper deposition is used to build various structures including TSV, RDL, Pillars, and Micro and Mega Bumps. Those processes utilize plating solutions that contain inorganic components and organic additives [2]. During the electroplating process, the additives can partially transform into compounds that are so-called breakdown products. The presence of such breakdown products can interfere with the electrochemical analysis of organic additives. This article presents results of plating tests that show the influence of freshly produced breakdown products on analysis of organic additives. In addition, several options to eliminate this effect are presented.

Key words

Analysis, CVS, Copper, Plating.

I. Introduction

The composition of electroplating baths is dependent on the types of features that are being plated. Larger features such as TSV and pillars typically require higher copper concentrations, while for RDL lower copper concentrations are preferred. The concentration of acid can vary too, but to a lesser extent, and concentrations of chloride ion are typically set around 50 ppm. The main differences in bath compositions are related to concentrations and type of organic additives used for plating. There is a variety of organic additives and additive packages offered by specialty chemical suppliers. Those additive packages may include up to four organic compounds. These materials are mostly proprietary, but the following examples of such additives are publicly known: Polyethylene Glycol (PEG), bis (3-sulfopropyl) disulfide (SPS) and Janus Green B (JGB). They are used as Suppressor, Accelerator, and Leveler respectively [2].

For better maintenance of plating bath composition, various bleed & feed schemes are used. These procedures are targeted to keep baths in control and reduce accumulation of by-products generated during electroplating processes. However, analytical feedback is crucial for bath maintenance, even with relatively high bleed and feed rates. The analyzed concentration values are used for fine-tuning of bath composition and adjustment of dosing rates for individual bath components.

Some by-products generated in copper plating baths during the deposition process will interfere with the analysis of organic additives. If the by-products are electrochemically active and the CVS technique is used for analysis, these species can alter analytical signals, consequently affecting final results. Understanding those effects is necessary in the development of accurate electrochemical analysis methods for determination of organic additives.

This development primarily addresses the effect of electrochemically active by-products of SPS (Accelerator) on analyses of all organic components in copper plating baths. The breakdown mechanism of SPS is quite complex and can lead to the formation of multiple by-products [3]. SPS can be broken down to its monomer MPS (mercaptopropane sulfonic acid) when it is electrochemically reduced on the cathode (wafer) of the plating tool. The freshly reduced MPS can form thyolate complex with copper (I). We studied the effect of MPS on the analysis of SPS as well as Suppressor and Leveler. When MPS is dosed into the bath, it acts as a potent Accelerator and cannot be electrochemically separated from the original SPS compound. However, when free MPS is in solution, it can be converted back to SPS if it reacts with oxidizer. To better understand this process, we studied possible reactions of MPS in the presence of various strong oxidizers such as ozone, oxygen, and hydrogen peroxide. The possible effects of oxidizers on SPS were also studied. It was found that the concentration of oxidizer must be optimized to successfully convert all MPS back to SPS without an impact on the actual SPS present in the bath. This article is the first in a series of publications that present the effect of various oxidizers used to convert Accelerator by-products and avoid their effect on the electrochemical analysis of organic additives used in electroplating.

II. Experimental Details

Chemicals and Materials - Solutions were prepared with sulfuric acid (Fisher), Copper Sulfate penta-hydrate (Sigma-Aldrich), and hydrochloric acid (Fisher). Organic additives (MPS and SPS) were obtained from Raschig GMBH. Other organic additives (PEG M.W. 3500-4500 g/mol and Janus Green B) were obtained from Sigma-Aldrich.

Instrumentation - Analyses were performed using an ECI QualiLab QL-10 bench top plating bath analyzer. A 4 mm Platinum Rotating Disk Electrode, an Ag/AgCl electrode with 0.1 M KCl junction solution, and a stainless steel rod counter-electrode comprised the three-electrode system. For plating tests, GwINTEK rectifier and Kokour A83 agitator were used.

Procedures - All three organic components were analyzed using general Cyclic Voltammetric Stripping analytical methods. These procedures are capable of providing analytical results that are accurate to within 5% of expected values. Plating experiments were performed in plating baths where 3 x 4 inches of pure copper cathode and phosphorized copper Hull cell anode were installed. During the plating, the solution was agitated with a linear movement of a paddle. 0.5, 2 and 5 Ah/L of electricity had passed through plating solution during aging test. In this article, the results after maximum 5 Ah/L plating are reported.

III. Results and Discussion

During electroplating, it is expected that the Accelerator and Leveler will be partially consumed in the bath while Suppressor concentrations remain virtually unchanged due to the nature of these organic materials [2]. To estimate the aging effect on electrochemical analysis, plating solutions were tested before and after plating.

Table 1. Effect of Bath Components on Plating Peak

Component	Fresh Bath	After Plating	24h After
Suppressor	1.0	0.95	0.96
Accelerator	1.0	1.3	0.74
Leveler	1.0	Not detected	0.95

As shown in **Table 1**, Suppressor component (PEG) is not sensitive to aging while obtained concentration values for Accelerator and Leveler appear to change significantly. Note that this bath was not dosed during the electroplating process, thus no increase of concentrations of Accelerator or Leveler was expected. Changes in the concentrations of Accelerator or Leveler must be investigated and understood as they appeared to be unexpected.

According to the following equation of reaction (1), the reduction of Accelerator (SPS) can occur on the cathode while plating:

$$\text{SPS} + 2\text{H}^+ + 2\text{e}^- \Leftrightarrow 2\text{MPS} \qquad (1)$$

The electrochemical effects of pure SPS versus MPS were studied by injecting them into the copper plating solution saturated with PEG. To minimize possible changes in the activity of tested materials, both solutions were prepared immediately prior to the test. **Fig. 1** shows the results of this comparison study.

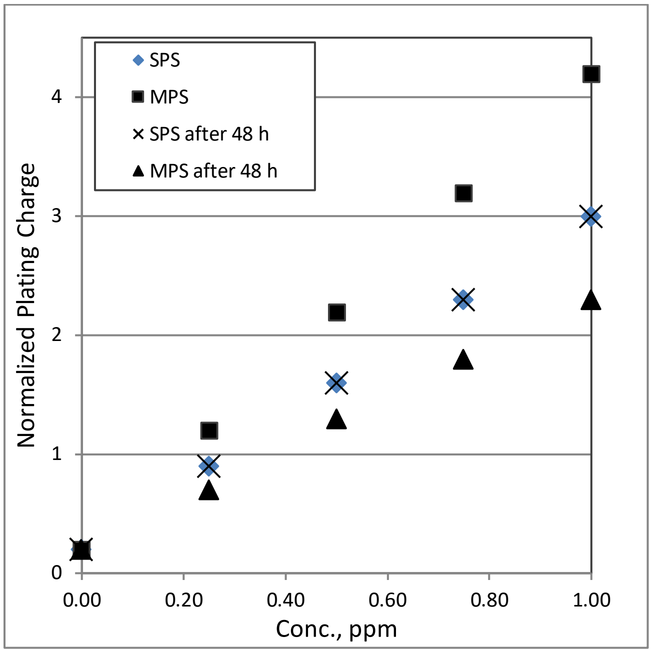

Fig. 1. Time effect on electrochemical responses of MPS and SPS

As shown in **Fig. 1**, the SPS component remains stable when mixed with other bath components, while MPS lost its accelerating ability, in agreement with equation (1) and consistent with the natural oxidation of MPS.

The dissolved oxygen plays an important role in conversion of MPS back to SPS. This suggests that the rate of this reaction may be intensified in the presence of stronger oxidants or by increasing the concentration of dissolved oxygen in the plating solution. The effect of dissolved oxygen on the stability of SPS breakdown products was previously described [3]. The dimerization of MPS occurs according to the following equation of reaction (2):

$$2MPS + \frac{1}{2} O_2 \Leftrightarrow SPS + 2H_2O \qquad (2)$$

It has also been described that the dissolved oxygen can oxidize copper (I) – thiolate complex, which is quite stable in the absence of oxygen. From an analytical process standpoint, oxygen appears to be an ideal reagent for converting MPS back to SPS. It can either be easily purged through solution before analysis or generated electrochemically *in situ*.

The other compounds can be used as oxidants as well. The list of possible oxidants is summarized in **Table 2**. As this table indicates, the redox potentials are quite different. Each component will cause oxidation of breakdown products and SPS itself.

Table 2. Oxidizing Agents

Oxidizing Agent	Redox Potential, V vs. SHE
Fe (III)	0.78
O_2	1.23
Ce (IV)	1.44
H_2O_2	1.78
$Na_2S_2O_8$	2.00
O_3	2.10

In this study, we screened the ability of Fe (III), oxygen, and hydrogen peroxide to oxidize SPS and MPS. More information about the cerium, persulfate, and ozone effect will be disclosed in subsequent publications.

The selectivity of oxidizer was tested. Ideally, selected materials should not cause oxidation of SPS. If oxidation is unavoidable, the oxidized amount of SPS should be negligible and within the accuracy of the analytical method. SPS can be oxidized by stronger oxidants. The standard redox potential of this reaction is 1.23 V vs SHE [3].

$$SPS - e \Leftrightarrow \text{Mono-ox } SPS \qquad (3)$$

Based on the standard potential values, it can be suggested that the original SPS compound may be affected if oxidizers [except Fe (III) and possibly oxygen] would be injected into the plating solution for the purpose of MPS conversion. Therefore, tests were performed to validate the effect of each oxidizer on SPS and MPS.

Table 3 compares the effects of equivalent injections of different oxidizing agents. Each test was repeated twice to validate reproducibility of aging conditions and analytical results. To estimate the required amount of Fe (III), for example, the following equation of reactions can be used.

$$2MPS + 2\,Fe^{3+} \Leftrightarrow SPS + 2H^{+} + 2Fe^{2+} \qquad (4)$$

Similar equation of reactions can be used for other oxidants.

Table 3. Effect of oxidizers on Accelerator analysis

Component	Fresh Bath	After Plating
Fe (III)	1.00	0.95
Oxygen	0.99	0.94
H_2O_2	0.91	0.82

The Accelerator analytical results in **Table 3** indicate that both Fe (III) and oxygen, when purged through fresh plating solution for 10 minutes, do not affect the Accelerator response. This suggests that SPS remains in its original state and can be accurately analyzed using electrochemical techniques.

At the same time, injection of a calculated amount of hydrogen peroxide (based on **Table 1** data) reduces the active amount of Accelerator, suggesting that the reaction described by equation (3) occurred. The concentration of hydrogen peroxide may be optimized to reduce its effect on SPS. However, hydrogen peroxide may not serve as an effective oxidizer of SPS by-products due to the lack of selectivity between MPS and SPS.

The data obtained from solution after plating indicates that either oxygen or Fe (III) reduces the effect of active by-products of SPS on the analytical results. Both oxidizers will be investigated further as reagents for analysis of heavily aged plating solutions that exhibit a presence of Accelerator by-products.

The Leveler results can also be distorted by the presence of Accelerator by-products in the plating solution. The same solutions treated with oxidizers were analyzed for Leveler concentrations. These analytical results are presented in **Table 4**.

Table 4. Effect of oxidizers on Leveler analysis

Component	Fresh Bath	After Plating
Fe (III)	1.01	0.99
Oxygen	1.01	0.99
H_2O_2	1.12	1.10

Again, both Fe (III) and oxygen do not affect the results of Leveler in fresh baths while hydrogen peroxide clearly alters the electrochemical behavior of the Leveler component. This effect must be understood better. The results show that the increase in concentration is due to interactions of H_2O_2 with both Accelerator and Leveler. To understand this behavior, more experiments will be conducted. This information will be published in the next part of this article.

IV. Conclusion

Accelerator by-products that form during electroplating can affect analytical results for Accelerator and Leveler. Several compounds were evaluated to eliminate this effect. The following two options are suggested: 1) Purging of the aged bath with pure oxygen for 10 minutes, or 2) injection of Fe (III) ion. Both compounds do not react with the original organic additives and effectively oxidize freshly formed Accelerator by-products. More information will be disclosed in subsequent publications.

References

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