

## An Empirical Relation between the Plating Process and Accelerator Coverage in Cu Superfilling

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The effects of plating process on the surface coverage of the accelerator were investigated in terms of Cu superfilling for device metallization. When a substrate having 500 nm-wide trench patterns on it was immersed in an electrolyte containing poly(ethylene glycol) (PEG) –chloride ion (Cl<sup>-</sup>) –bis(3-sulfopropyl) disulfide (SPS) additives without applying deposition potential for such a time of about 100s, voids were generated inside of the electrodeposit. In time-evolved electrochemical analyses, it was observed that the process (immersion without applying potential) in the electrolyte led to the build-up of high initial coverage of SPS-Cl on the surface, resulting in the fast saturation of the coverage. Repeated experiments suggested that the fast saturation of SPS-Cl failed in superfilling while a gradual increase in the SPS-Cl coverage through competition with initially adsorbed PEG-Cl enabled it. Consequently, superfilling was achievable only in the case of applying the plating potential as soon as the substrate is dipped in an electrolyte to prevent rapid accumulation of SPS-Cl on the surface.

**Key Words** : Cu, Electroplating, Superfilling, Additives, Coverage

### Introduction

Cu electroplating is one of the most important process parts in the fabrication of microelectronics interconnection, such as integrated circuits (ICs) and printed circuit boards (PCBs).<sup>1-4</sup> In the process, it is required to make Cu superfilling which means a complete filling of patterned structures without leaving voids. In this purpose, organic additives are generally added to the plating electrolyte. The superfilling with poly(ethylene glycol) (PEG) and bis(3-sulfopropyl) disulfide (SPS) combined with Cl ion is a well-known phenomenon, and many researches have been focused on the evaluation of additive mechanism and its effect on electrodeposit.<sup>1,5-16</sup> Moreover, numerical models established by Moffat *et al.* and West *et al.* have simulated the superfilling phenomena with a bump formation.<sup>7-9,16</sup> However, though there have been many reports concerning the superfilling phenomena, the complex behavior of the additives in couple with the factors originated from the surface potential, surface chemistry between ions and molecules, and substrate properties are still in question.

For example, superfilling is sometimes hard to achieve even with the general experimental conditions described by precedent papers, such as proper composition of sulfuric acid, copper sulfate, PEG-Cl-SPS additives, and proper plating potential and current. This is because there may be additional factors for superfilling that are as critical as the other conditions.

In this study, we empirically observed one of the factors, which is strongly related to the changes in surface SPS coverage. In doing this, we have found that the initial

coverage of SPS may determine the filling profiles, and the coverage was controllable as well. Based on this, we proposed a general starting procedure of Cu plating to achieve superfilling.

### Experimental

The substrate was a trench-type (with a line width of 500 nm and a depth of 1250 nm) patterned Si wafer with PVD Cu (100 nm)/CVD TiN (10 nm)/PVD Ti (15 nm) multilayer on it. An electrolyte was composed of 0.25 M CuSO<sub>4</sub>·5H<sub>2</sub>O, 1.0 M H<sub>2</sub>SO<sub>4</sub>, and deionized water. A combination of 88 μM PEG (Mw 3400, Aldrich), 1 mM NaCl, and 50 μM SPS (Raschig GmbH) was added in the electrolyte as a suppressor-accelerator additive system. Cu electroplating was conducted with a 99.9% Cu wire as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. A plating potential was -200 mV (*vs.* SCE). The plating potential was applied either i) just before or ii) after the substrate was immersed in the electrolyte, using PAR 263 (EG&G Princeton Applied Research Corporation) potentiostat.<sup>16,17</sup> A deposit area was 1 cm<sup>2</sup>. The Cu electrodeposit was rinsed with deionized water and dried with a N<sub>2</sub> stream. The deposit profile was analyzed using a field emission scanning electron microscopy (FESEM, JEOL, JSM-6330F).

In order to analyze the adsorption behavior of additives and its effect on the subsequent plating, chronoamperometries were performed on a Cu rotating disk electrode (RDE, 0.2 cm<sup>2</sup>) with rotating speed of 300 rpm. In the analyses, -200 mV (*vs.* SCE) was applied constantly for 300 s. The RDE surface was prepared with polishing with

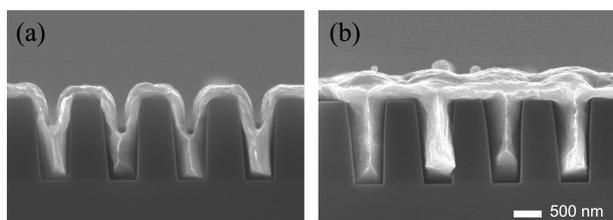
SiC paper and derivitizing of organic additives prior to the electrochemical analyses. Derivitization, a method to make an additive layer on the electrode surface,<sup>15,17</sup> was conducted with dipping of the polished surface in water containing additives with the same concentration as in the plating electrolyte. The derivitization time was controlled in order to change the coverage of additives on the RDE surface.

## Results and Discussion

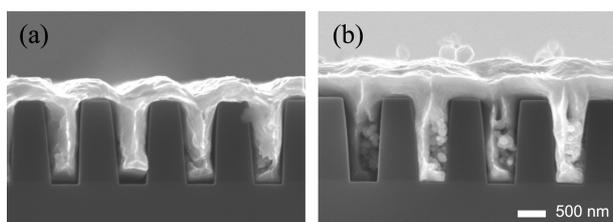
A representative Cu superfilling achieved by using the PEG-Cl-SPS additive system is presented in Figure 1. Preferential deposition at the trench bottom, known as the bottom-up process (Fig. 1(a)), and subsequent bump formation at the top of the trenches (Fig. 1(b)) were clearly observed. In this case, the plating potential ( $-200$  mV vs. SCE) was applied just before the substrate was dipped in the electrolyte (this process is now denoted as “hot immersion”<sup>18</sup>). When the potential was applied after the immersion (denoted as “cold immersion”), however, the trench was not filled even with the same additive system and the plating condition (Fig. 2). It was due to the damage on the seed layer by Cu corrosion in the acidic plating electrolyte.<sup>19</sup> The step coverage of PVD seed is intrinsically poor,<sup>9,20-26</sup> and the seed

damage deteriorate the formation of continuous film (note that the voids are populated at the side walls). As the immersion time without applying potential is increased (Fig 2(b)), the void density significantly increased due to the severe corrosion of the seed. In contrast, the hot immersion makes the seed layer to be negatively polarized and protected cathodically,<sup>16,20,23</sup> because cupric ion is not thermodynamically stable in a state of negative potential. Although the native oxide existed on the surface, it did not seriously affect electroplating due to the too thin layer to block the electron transfer. The oxide layer can also be reduced coulometrically during the deposition.<sup>27</sup>

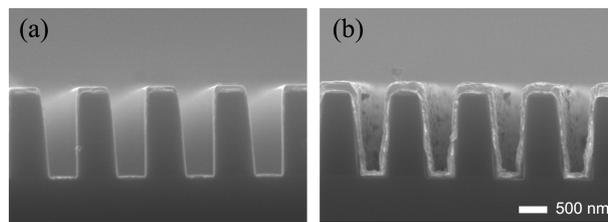
To eliminate the problems originated from the corrosion of very thin seed layer, the thickness of the seed layer was enhanced by plating about 100 nm Cu conformally on the side wall and the bottom of the trench in the identical plating solution with low acid contents (0.2 M of sulfuric acid) with a current density of 4 mA/cm<sup>2</sup> for 150s. As shown in Figure 3, after the enhancement the side wall thickness was increase from 32 nm to 127 nm with excellent step coverage of 0.6 (from 0.3). The enhanced seed was further used in the superfilling and the results are depicted in Figure 4. As expected, the hot immersion is always capable of superfilling (Fig. 4 (a)) regardless of seed layer enhancement. However, in the case of cold immersion, despite of the seed layer repairing, voids still exist at the center of the deposit (Fig. 4(b) and (c)). As the time duration between cold immersion and the moment of applying potential increases the void size is also increased. It should be noted that the position of void is shifted from the side wall to the center of the deposit. This implies that the void formation in this case is related to the additive function rather than a problem of seed layer. (Note that the side wall void most happens due to the discontinuity of the seed layer while center void is generated in the case of no additives or the malfunction of the additives.) The cold



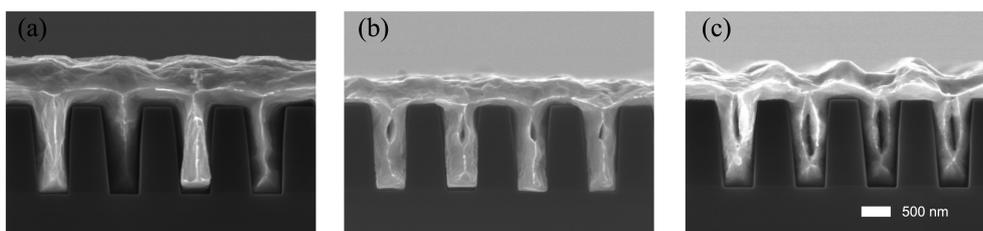
**Figure 1.** Cross-sectional FESEM images of hot immersion electrodeposited Cu for (a) 150 s and (b) 350 s with the PEG-Cl-SPS system. The plating potential was  $-200$  mV (vs. SCE).



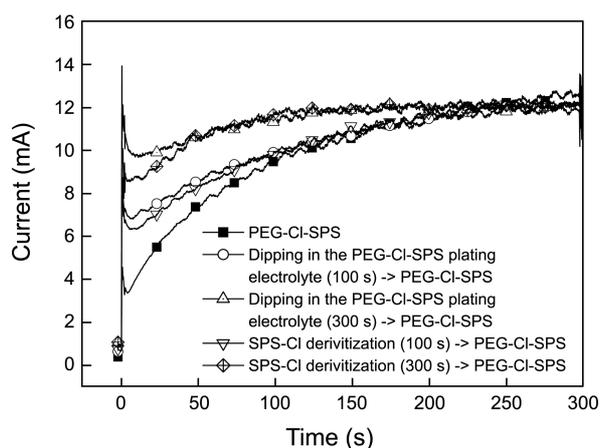
**Figure 2.** Cross-sectional FESEM images of cold immersion electrodeposited Cu for 350 s with the PEG-Cl-SPS system. The immersion time is (a) 100 s and (b) 300 s.



**Figure 3.** Cross-sectional FESEM images of the Cu seed layer (a) before and (b) after seed layer repairing.



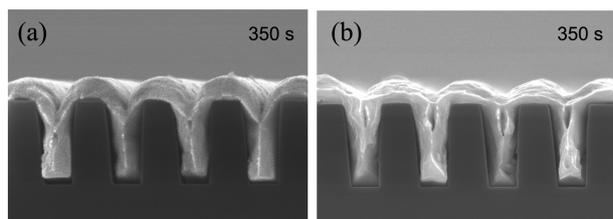
**Figure 4.** Cross-sectional FESEM images of Cu electrodeposited for 350 s on the repaired seed layers. (a) hot immersion, (b) cold immersion with immersion time of 100 s, and (c) cold immersion with immersion time of 300 s, respectively.



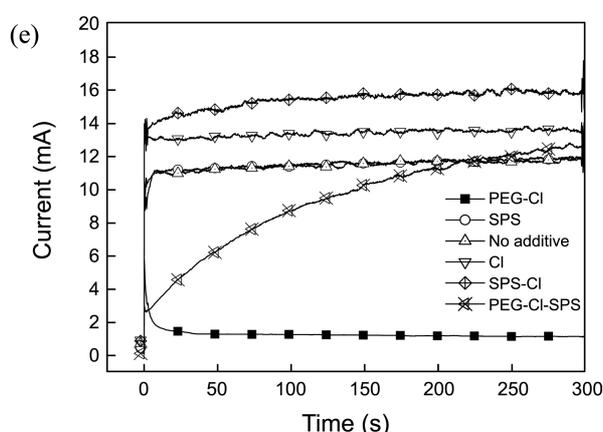
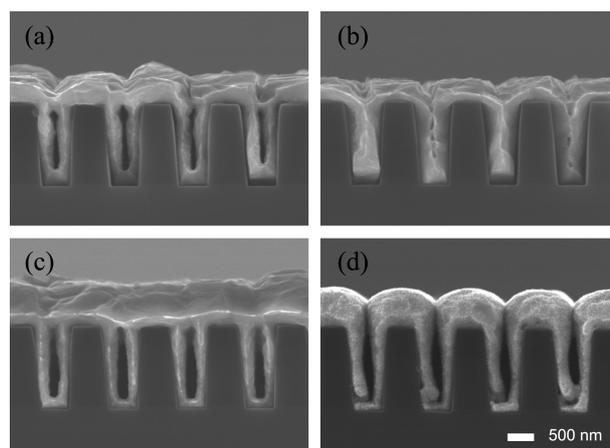
**Figure 5.** Chronoamperometry of the PEG-Cl-SPS system on rotating disk electrode (RDE). The rotating speed was 300 rpm and the applied potential was  $-200$  mV (vs. SCE). The SPS-Cl derivitization solution was composed of 1 mM NaCl, 50  $\mu$ M SPS, and deionized water.

immersion may have negative impact on the proper function of the additive system.

The additive behaviors according to the immersion condition were monitored with chronoamperometry on the RDE as shown in Figure 5. In the PEG-Cl-SPS system, the chronoamperometry showed a typical current behavior of slow rising from 3.5 mA to a saturated current (about 12 mA) in 250 to 300 s. This represents the saturation of the accelerator (SPS-Cl) coverage through the competitive replacement of the suppressor (PEG-Cl).<sup>28,29</sup> In the case of cold immersion of RDE, the initial current was larger than that of the hot immersion case. Longer duration (100 to 300 s) between the dipping and the moment of applying potential led to a higher initial current. The same elevation in the initial current was also observed on the RDE derivitized with SPS-Cl. The derivitization with SPS-Cl increased the initial current in proportion to the derivitization time like the cold immersion case. The derivitization with SPS-Cl was also incapable of superfilling during the subsequent plating in the PEG-Cl-SPS system as shown in Figure 6. With this we can partially conclude that the cold immersion has similar effect with the derivitization. The adsorption of the accelerator by the immersion in the plating electrolyte also has been presented in other research.<sup>30</sup> Therefore, the immersion prior to electroplating (cold immersion) may increase the surface



**Figure 6.** Cross-sectional FESEM images of Cu electrodeposited with the PEG-Cl-SPS system on a seed layer derivitized with SPS-Cl for (a) 100 s and (b) 300 s. The number shown is the plating time.

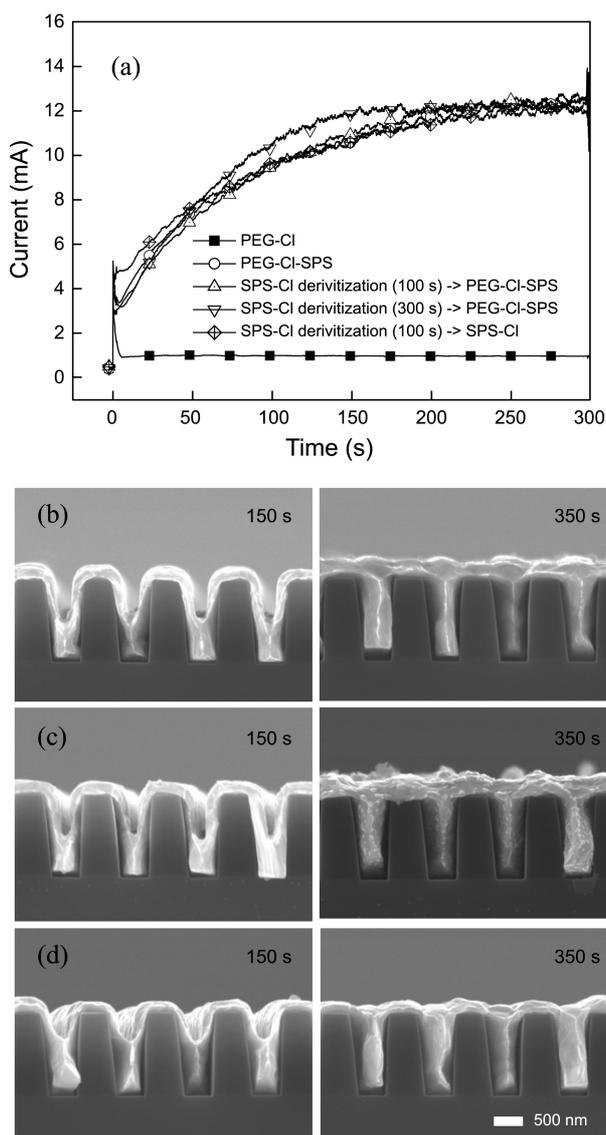


**Figure 7.** Cross-sectional FESEM images of electrodeposited Cu in the electrolyte containing (a) no additives, (b) PEG-Cl, (c)  $\text{Cl}^-$ , and (d) SPS-Cl. (e) Chronoamperometry on RDE according to the additive combination.

coverage of SPS-Cl, likewise the derivitization, and the initially high coverage of SPS-Cl has the negative impact on superfilling.

Generally accepted superfilling models are based on the local increase in the plating rate at the bottom corners of the trench with the surface accumulation of the accelerator due to the area reduction.<sup>7,8,10,16</sup> The surface coverage of accelerator should be gradually increased by substituting the suppressor. Therefore, the superfilling could not be achieved by using a single additive as shown in Figure 7(a) to (d). This is due either to the full suppression (suppressor only case) or to the rapid increase in the initial current in the case of  $\text{Cl}^-$  or SPS-Cl (accelerator only case) as shown in the chronoamperometry (Fig. 7(e)). The superfilling is only achievable in the case of low initial current followed by gradual increase in the current (suppressor-accelerator case). This implies the initially high surface coverage of PEG-Cl (low initial current) and its substitution by SPS-Cl (gradual rising in the current) is crucial to the superfilling. The fast saturation of the accelerator coverage does not allow the superfilling.

The significance of the initial formation of a suppressing layer and the gradual substitution by the accelerator was further studied. Figure 8 exhibits the evaluation of the effects



**Figure 8.** (a) Chronoamperometry of the PEG-Cl-SPS system on rotating disk electrode (RDE). The PEG-Cl derivitization solution was composed of 88  $\mu\text{M}$  PEG, 1 mM NaCl, and deionized water. Cross-sectional FESEM images of electrodeposited Cu with the PEG-Cl-SPS system on the seed layer derivitized with PEG-Cl for (b) 100 s and (c) 300 s. (d) Cross-sectional FESEM images of electrodeposited Cu with the electrolyte containing SPS-Cl on the seed layer derivitized with PEG-Cl for 100 s.

of PEG-Cl derivitization by chronoamperometry and filling profile. The derivitization using PEG-Cl on the Cu surface had no difference in the current behavior (Fig. 8(a)) and filling profile (Fig. 8(b) to (d)) compared to the conventional PEG-Cl-SPS system, regardless of the derivitization time. This clearly suggests that the PEG-Cl layer was formed at the early stage of the immersion in the case of PEG-Cl-SPS system. This was also confirmed by the fact that the current response of the Cu surface derivitized with PEG-Cl in the SPS-Cl system (Fig. 8(a)) was exactly the same with that of the non-derivitized surface in the PEG-Cl-SPS system. The displacement occurred quite slowly compared to the fast saturation of accelerator coverage in the absence of PEG-Cl

(Fig. 8(a) vs. Fig. 7(e)). That is, the PEG-Cl suppressing layer was slowly detached by SPS-Cl whereby the coverage of SPS-Cl was maintained below the saturated value for long time (around 300 s).

Consequently, PEG-Cl inhibits the fast saturation of SPS-Cl coverage, and SPS-Cl increases its coverage gradually in competition with PEG-Cl. In the case of cold immersion, the coverage of SPS-Cl was initially elevated and quickly saturated. The saturated SPS-Cl coverage on the entire seed surface may not respond to the "Curvature Enhanced Accelerator Coverage" phenomena,<sup>16</sup> which is related to the gradual increase in the accelerator coverage at the bottom corners of the pattern by area reduction as the plating proceed. As a result, the bottom-up process ceased and the voids were formed in the trench. To achieve superfilling, therefore, electroplating should be started in a very short time from the moment of immersion (less than 50 s, which is empirically determined but may vary according to the pattern size and additive concentration) or hot immersion method to prevent the initial high-level SPS-Cl coverage. The hot immersion provides not only superfilling but also protection from seed layer damage.

## Conclusion

We have tested two deposition modes; hot immersion (immersion of the seed with applying the deposition potential) and cold immersion (immersion without applying potential). Using the conventional 88  $\mu\text{M}$  PEG -1 mM Cl-50  $\mu\text{M}$  SPS system, only the hot immersion was capable of superfilling. Various sets of filling experiments and electrochemical analysis revealed that the initial coverage of SPS-Cl was crucial in determining the success of the superfilling. For the proper working of superfilling mechanism, prevention of initial saturation of SPS-Cl coverage was necessary and the hot immersion method was effective in doing that, while cold immersion with about 100 s or more of cold state was vulnerable to the fast saturation of SPS-Cl coverage. The tolerant time of cold state may vary according to process factors such as the pattern size and additive concentration

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