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## Triblock Copolymers as Suppressors for Microvia Filling via Copper Electroplating

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In this work, ethylene-propylene-ethylene (EPE) oxide triblock copolymers were found to be effective suppressors for microvia filling during copper electroplating. The studied EPE copolymers were divided into two groups according to their solubility and compositions. The first group was composed of EPE 1000, EPE 2000, and EPE 3500, and the second group contained EPE 2450, EPE 2900, and EPE 8000. In particular, the function of the triblock copolymer suppressors (e.g. EPE 2900) and their synergistic effect with other additives during copper electroplating were studied by galvanostatic measurements, suggesting that the suppression strength was greatly dependent on  $\text{Cl}^-$ . In addition, cyclic voltammetry (CV) measurements indicated that a given suppressor in the plating bath required an optimal  $\text{Cl}^-$  concentration to realize the strongest suppression strength. Then the filling performance of the plating bath using different suppressors was systematically compared by galvanostatic measurements and filling plating experiments in the plating bath with a fixed  $\text{Cl}^-$  concentration (60 ppm), an optimal  $\text{Cl}^-$  concentration, and a wide operation window of  $\text{Cl}^-$  respectively. These experimental analyzes indicated that EPE 2000 and EPE 2900 were the best suppressors in the first and second group, respectively. The relevant mechanism of triblock copolymer suppressors for microvia filling was discussed.

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During the printed circuit boards (PCBs) manufacturing, the interconnection of circuits or electronic components between different layers was realized via microvia filling using copper electroplating.<sup>1,2</sup> In addition, stacked microvias in intergrated circuit (IC) substrates to connect the contact points of IC chips were used in mass-production for minimizing the size of the packaging substrates.<sup>3,4</sup> In both processes, the microvias should be fully filled with deposited copper without void or seam in an ideal mode so called “superfilling” or “bottom-up deposition”.<sup>6-11</sup>

To meet above requirements, two types of additives, a suppressor and an accelerator, should be present in the copper plating bath simultaneously. The currently used accelerators, such as 3-mercaptopropanesulfonate (MPS) and bis(3-sulfopropyl) disulfide (SPS), can significantly enhance copper deposition at the bottom of the microvia with the assistance of chloride ions.<sup>12-14</sup> On the contrary, the suppressors, such as polyethylene glycol (PEG),<sup>15-18</sup> polypropylene glycol (PPG) and the triblock copolymers of PEG and PPG,<sup>19-21</sup> commonly adsorbed on the board surface and inhibited copper deposition due to the formed barrier layer. Thus, the accelerating effect at the microvia bottom and the inhibiting effect on the board surface eventually led to the superfilling of microvias. To improve the microvia filling performance, a leveler, such as Janus Green B (JGB), was usually introduced into the plating bath.<sup>22,23</sup>

To date, many additive combinations used for microvia filling such as PEG-Cl-SPS,<sup>12</sup> PEG-Cl-MPS,<sup>17</sup> PEG-Cl-MPS-JGB,<sup>23</sup> PEG-Cl-SPS-DB,<sup>24</sup> etc, had been reported. Interestingly, nearly all of the suppressors used in these reported literatures was PEG.<sup>1-18,22,23</sup> However, it was found that the inhibiting effect on copper deposition caused by PEG was minor if the  $\text{Cl}^-$  was absent. In other words, the suppression strength would be enhanced with the concentration of  $\text{Cl}^-$  up to a limit at a fixed PEG concentration.<sup>25</sup> Cathodic polarization and electrochemical impedance spectroscopy (EIS) analyzes suggested that the inhibiting effect of PEG was potential-dependent and the existence of  $\text{Cl}^-$  could widen the adsorption and desorption potential ranges of PEG.<sup>26</sup> The possible complex adsorbed on the cathode surface for inhibiting  $\text{Cu}^{2+}$  deposition was  $\text{PEG-Cu}^+-\text{Cl}$  that was determined by surface-enhanced Raman spectroscopy.<sup>27</sup>

Compared to PEG, the triblock copolymers of ethylene oxide (EO) - propylene oxide (PO) - ethylene oxide (EO) would lead to enhanced performances in microvia filling due to their special structures and easily controlled ratios of EO/PO. West and his co-workers studied the adsorption and desorption characteristics of PEG, PPG, and

PEG/PPG copolymers during copper plating and it was concluded that most suppressors adsorbed to copper surface at similar rates under galvanostatic plating conditions except for PPG 2000.<sup>19</sup> However, significant differences in their desorption behaviors were observed, greatly dependent on their molecular weights, compositions of the molecule, and the end groups. West et al., also studied the filling performance of the low acid copper plating bath using PEG 3350, PPG 725, and EPE 2000 as the suppressors and suggested that EPE 2000 could result in the most rapid filling due to its highest suppression strength.<sup>20</sup>

In this work, two groups of triblock copolymers comprised of ethylene oxide - propylene oxide - ethylene oxide (EPE) with different molecular weights and EO/PO ratios were systematically studied as the suppressors in copper electroplating for microvia filling. The first group was alcohol-soluble (EPE 1000, EPE 2000, and EPE 3500) and the second group was water-soluble (EPE 2450, EPE 2900, and EPE 8000). PEG with a molecular weight of 6000 (PEG 6000) was used as a reference for a comparison. Galvanostatic measurement was employed to study the function of these triblock copolymers (e.g. EPE 2900) and their synergistic effect with other additives. Cyclic voltammetry (CV) was used to determine the optimal  $\text{Cl}^-$  concentration for each suppressor. The filling performances of the plating baths using different suppressors were systematically compared by galvanostatic measurements and filling plating experiments in the plating bath as a function of  $\text{Cl}^-$  concentration. The correlation of the suppression strength with the corresponding filling performance for these triblock copolymer suppressors at the optimal  $\text{Cl}^-$  concentration was discussed in-depth.

### Experimental

**Microvia filling by copper electroplating.**— PCBs with microvias fabricated by  $\text{CO}_2$  laser ablation were used as testing samples for the microvia filling plating. Here the PCBs were composed of dielectric layer (epoxy resin reinforced by glass fiber) and copper foil. The size of the testing sample was  $5 \times 9 \text{ cm}^2$ . And the number of the microvias in each sample was 600. The diameter and depth of the microvias are  $150 \mu\text{m}$  and  $75 \mu\text{m}$ , respectively. Prior to filling plating, the sidewall of the microvia was metallized by electroless copper plating for 2–3  $\mu\text{m}$  copper film. In the plating experiment, phosphorus-containing (0.03–0.065 wt%) copper plate ( $6 \times 10 \text{ cm}^2$ ) was used as the anode and directly placed in the plating bath with a working volume of 1500 mL. The testing samples were first activated in 10 wt%  $\text{H}_2\text{SO}_4$  solution for 1 min, and then pre-dipped in the plating bath for 5 min so as to wet the microvias thoroughly. The current density for copper plating

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**Table I. Detailed formulation of the suppressors.**

The Suppressors	The first group			The second group			
	EPE 1000	EPE 2000	EPE 3500	EPE 2450	EPE 2900	EPE 8000	PEG 6000
Corresponding Trade Name	L-31	L-61	L-101	L-62	L-64	L-68	PEG-6000
Molecular Weight (g/mol)	1000	2000	3500	2450	2900	8000	6000
The Ratio of EO (wt%)	10	10	10	20	40	80	100
Solubility in Water at 23°C (10 wt% solutions)	- <sup>a</sup>	-	-	+ <sup>b</sup>	+	+	+

<sup>a</sup>- Insoluble;<sup>b</sup>+ Soluble

was controlled at 2 A/dm<sup>2</sup> and plating time was 100 min. During electroplating, agitation by continuous air bubble flow was sustained to ensure an efficient mass transfer.

The electrolyte used for microvia filling plating and the relevant electrochemical measurements was prepared from CuSO<sub>4</sub> · 5H<sub>2</sub>O (220 g/L) and H<sub>2</sub>SO<sub>4</sub> (55 g/L). The added additives were Cl<sup>-</sup> (added as NaCl), SPS (3 ppm), Janus Green B (JGB, 4 ppm) and the studied suppressor. All of the triblock copolymers were obtained from BASF with the structure of EO-PO-EO (EPE) and different molecular weight including EPE 1000, EPE 2000, EPE 3500, EPE 2450, EPE 2900, and EPE 8000. The detailed formulation was listed in Table I. According to their different solubility in water and EO/PO ratios, the studied triblock copolymers were divided into two groups: first group dissolved in alcohol (EPE 1000, EPE 2000, and EPE 3500); the second dissolved in water (EPE 2450, EPE 2900, and EPE 8000). PEG 6000 that had a better filling performance demonstrated by Dow<sup>12</sup> was used as a reference. According to its structure, PEG 6000 can be regarded as a triblock copolymer with 100 wt% EO segments. The temperature of the plating solution was maintained at 25 °C. The microvia filling performance of the plating bath containing various suppressors was examined by cross-sectional views of the microvias using optical microscopy (DFC290, Leica). The preparation of the cross-sectional sample can be divided into three steps. The first step was to fix the PCB sample using crystal epoxy. The second step was to abrade the microvias using #180, #400, #1200, #2000 SiC papers. Then the sample was polished with Al<sub>2</sub>O<sub>3</sub> powder. The third step was to etch the sample in order to distinguish the electrodeposited copper film from the substrate copper foil. The etching solution was composed of 40 g/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 40 g/L NaCl, and 75 g/L H<sub>2</sub>SO<sub>4</sub>. To improve the reliability, the cross-sectional views of fifteen microvias were carefully observed for each PCB sample after filling plating.

**Electrochemical measurements.**— The optimal Cl<sup>-</sup> concentrations for different suppressors were analyzed by CV stripping (797 VA Computrace, Metrohm) instrument with automatic and continuous addition of Cl<sup>-</sup>. A platinum rotating disk electrode with a diameter of 3 mm and a platinum bar were used as the working electrode and the counter electrode, respectively. The reference electrode was Ag/AgCl (3.0 mol/L KCl) electrode, which was placed in a small teflon tube that contained 1 mol/L KNO<sub>3</sub> solution. The end side of the teflon tube was sealed with a porous polymer material. The rotation speed of the working electrode was fixed at 1000 rpm. The CV measurements were carried out with a negative-going sweep from 1.625 V to -0.250 V, followed by a positive-going sweep from -0.250 V to 1.625 V, at a scan rate of 0.1 V/s.

Galvanostatic measurements (GMs) and linear sweep voltammetry (LSV) tests were carried out on an electrochemical workstation (CHI 760D) in a three-electrode cell at a temperature of 25 °C. A platinum rotating disk electrode (Pt-RDE, Pine) with a diameter of 5 mm was employed as the working electrode. The counter electrode was a small copper bar, which was placed in a small glass tube that contained only the basic electrolyte without containing additives. The end side of the small glass tube was sealed with a porous polymer material to avoid possible contamination with these additives.<sup>1</sup> A

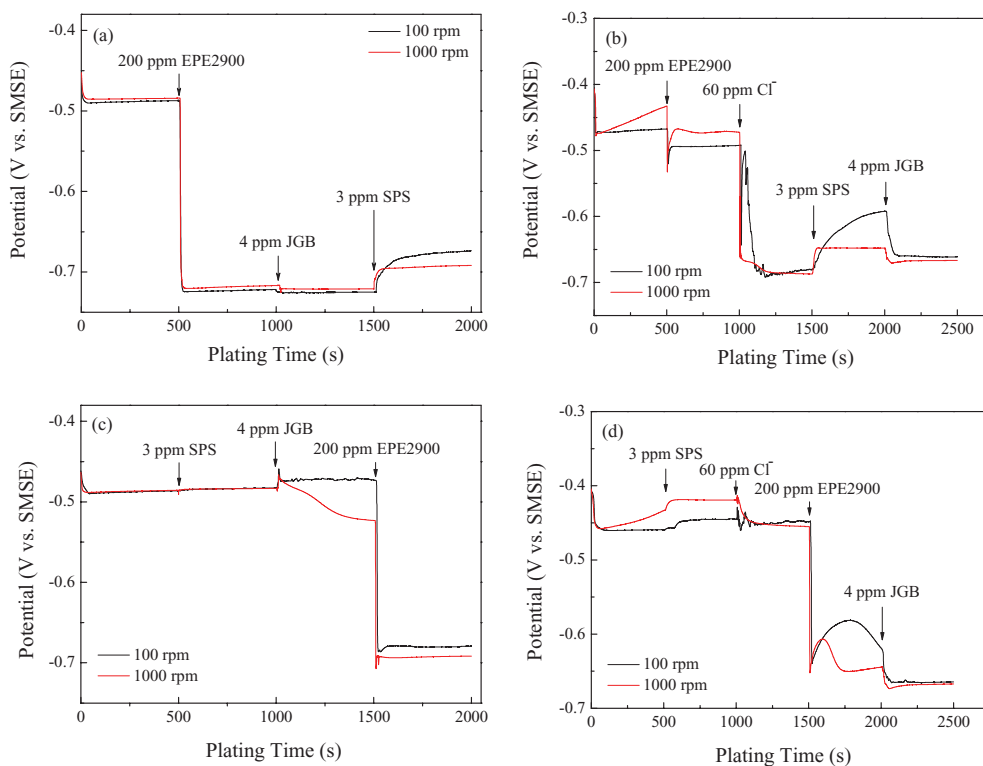
saturated mercury-mercurous sulfate electrode (SMSE) was used as the reference electrode. Before each electrochemical measurement, a thin copper layer with a thickness of 500 nm was deposited onto the Pt-RDE in the base electrolyte to prepare a Cu-RDE.

The GMs were performed at a current density of 2 A/dm<sup>2</sup> with the rotation speed of the Cu-RDE at 100 rpm and 1000 rpm respectively. According to the convection-dependent adsorption (CDA) mechanism,<sup>1,24,28</sup> the  $\Delta\eta$  value, an average of potential difference obtained by subtracting the potential measured at 1000 rpm from that measured at 100 rpm, can be used as an indicator of the filling performance. Larger  $\Delta\eta$  value usually indicated better filling performance. The LSV testing was conducted with a negative-going sweep from open circuit potential to -0.7 V vs. SMSE at a scan rate of 1 mV/s. The rotation speed of the Cu-RDE was 1000 rpm during the tests.

## Results and Discussion

**The function of the suppressor (EPE 2900) and its interactions with other additives.**— The function of EPE 2900 and its synergistic effect with other additives were studied using GMs by adding Cl<sup>-</sup>, SPS, EPE 2900, and JGB into the electrolyte successively at two different rotation speeds. As shown in Fig. 1a, the cathodic potential of the Cu-RDE was sharply decreased upon 200 ppm EPE 2900 was added no matter forced convection existed or not. This suggested that EPE 2900 can quickly adsorb onto the Cu electrode surface and then strongly inhibit subsequent copper deposition. Followed by adding 4 ppm JGB, the cathodic potential showed a slight decrease, indicating that JGB was able to further enhance the inhibiting effect of EPE 2900. On the contrary, when 3 ppm SPS was introduced into the plating solution, the potential exhibited an increase as expected, as the adsorbed EPE 2900 on the cathode surface was partly replaced by SPS. Interestingly, the potential increment at 100 rpm was larger than that at 1000 rpm, indicating that the adsorption of SPS could be facilitated in a relatively weak convection condition. In other words, SPS was more functional at the bottom of the microvia where forced convection was relatively weak. It was noted that, after the addition of SPS, the increasing potentials measured at 100 rpm was more slowly reached a plateau after hundreds of seconds, compared to the increase of potentials measured at 1000 rpm. Thus, the weaker the forced convection, the longer time needed to reach the equilibrium. This phenomenon indicated that the adsorption of SPS on the cathode by replacing adsorbed EPE 2900 was a sluggish process and influenced by the strength of forced convection. Comparing the two curves obtained at 100 and 1000 rpm in Fig. 1a, it could be seen that superfilling ( $\Delta\eta > 0$ ) did not occur until 3 ppm SPS was added into the plating solution.

As shown in Fig. 1b, the inhibiting effect on copper deposition caused by 200 ppm EPE 2900 was insignificant until the addition of 60 ppm Cl<sup>-</sup>, suggesting that the adsorption of EPE 2900 at the cathode could be greatly enhanced in the presence of Cl<sup>-</sup>. In the absence of Cl<sup>-</sup>, EPE 2900 could adsorb onto the cathode by van der Waals force and electrostatic interaction.<sup>26</sup> However, after the addition of Cl<sup>-</sup>, EPE 2900 can form a complex with Cl<sup>-</sup> and Cu<sup>+</sup> to (similar to PEG-Cl<sup>-</sup>-Cu<sup>+</sup>)<sup>26,27</sup> and finally adsorbed onto the cathode by intermolecular binding force. As mentioned before, adding of SPS was favorable of achieving the superfilling ( $\Delta\eta > 0$ ) due to its changing



**Figure 1.** GMs with the successive addition of various additives at two different rotation speeds: 100 and 1000 rpm. The basic electrolyte was composed of (a) and (c) 220 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 55 g/L  $\text{H}_2\text{SO}_4$  and 60 ppm  $\text{Cl}^-$ ; (b) and (d) 220 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 55 g/L  $\text{H}_2\text{SO}_4$ .

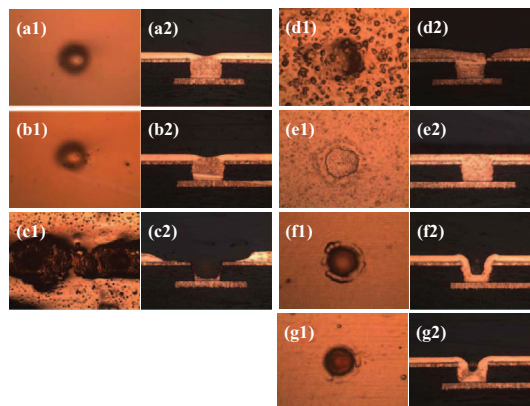
behavior at different forced convections. This experiment indicated that the superfilling could occur in the plating bath simultaneously containing EPE 2900,  $\text{Cl}^-$ , and SPS. The addition of JGB could enhance the inhibiting effect of EPE 2900, especially at weak forced convection.

The adding sequence of additive was rearranged as shown in Fig. 1c and 1d to further clarify the interaction among these additives. It can be seen from Fig. 1c that in the presence of  $\text{Cl}^-$ , the addition of SPS resulted in a slight and slow increase of the cathodic potential. It indicated that the adsorption of SPS onto the cathode was a slow process. However, in the absence of  $\text{Cl}^-$ , the addition of SPS led to a relative larger potential increase, as shown in Fig. 1d. Moreover, it can be noted that the addition of  $\text{Cl}^-$  can weaken the accelerating effect of SPS on copper deposition. Compared Fig. 1c with Fig. 1d, the cathodic potential sharply decreased after the addition of EPE 2900 no matter forced convection was weak or strong. However, the cathodic potential obtained at weak forced convection was more positive than that at strong forced convection. It suggested that the adsorbed SPS can be more easily replaced by EPE 2900 at strong forced convection than that at weak forced convection. In other words, the adsorption strength of SPS onto the cathode was stronger in a relatively weak convection condition.

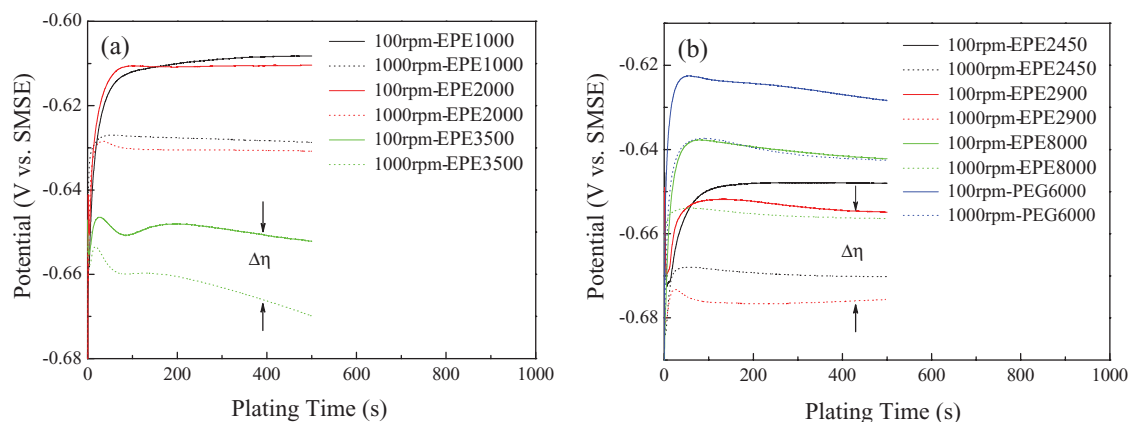
Based on these experiments, EPE 2900 exhibited a quick adsorption process and performed well on the surface of the PCB where forced convection was relatively strong. On the contrary, SPS showed a slow adsorption process and predominantly worked at the bottom of the microvias where forced convection was weak. In other words, in the presence of adsorbed EPE 2900, the adsorption strength of SPS onto the cathode at weak forced convection was stronger than that at strong forced convection. On the contrary, in the presence of adsorbed SPS, the adsorption strength of EPE 2900 at weak forced convection was weaker than that at strong forced convection. If JGB was present in the plating solution, the suppression strength of EPE 2900 on copper deposition can be enhanced due to their synergistic effect. Compared to SPS and JGB, this work also found that the inhibiting

effect of EPE 2900 on copper deposition was much more dependent on  $\text{Cl}^-$ .

*Filling performances of triblock copolymer suppressors at a high concentration (200 ppm) with a fixed  $\text{Cl}^-$  concentration of 60 ppm.*— In a typical copper electroplating formula containing a fixed  $\text{Cl}^-$  concentration of 60 ppm, the microvia filling performance was systematically investigated as a function of the type of triblock copolymer suppressor at a constant concentration of 200 ppm. As shown in Fig. 2, the plating bath using EPE 2900 as the suppressor offered the best filling performance and the resulting microvia was



**Figure 2.** Optical microscope images of microvias after electroplated in typical plating bath. The typical plating bath is composed of 220 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 55 g/L  $\text{H}_2\text{SO}_4$ , 60 ppm  $\text{Cl}^-$ , 3 ppm SPS, 4 ppm JGB and 200 ppm suppressor. The suppressors are: (a) EPE 1000, (b) EPE 2000, (c) EPE 3500, (d) EPE 2450, (e) EPE 2900, (f) EPE 8000, and (g) PEG 6000. 1 and 2 correspond to top views and cross-sectional views, respectively. All the images are magnified 200 $\times$ .



**Figure 3.** GMs performed in the plating baths using different suppressors at two different rotation speeds: (a) the first group of suppressors; (b) the second group of suppressors. The plating bath is composed of 220 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 55 g/L  $\text{H}_2\text{SO}_4$ , 60 ppm  $\text{Cl}^-$ , 3 ppm SPS, 4 ppm JGB and 200 ppm suppressor.

fully filled by deposited copper without void or dimple. The filling performance measured with the plating baths containing EPE 1000 and EPE 2000 was comparable and a small dimple was observed with both of them.

In contrast, as shown in Fig. 2(c2), superfilling was not observed in the microvias when EPE 3500 was used as the suppressor. There was hardly any copper deposited near the mouth of the microvias. Moreover, many pin-holes could be found on the deposited copper film (Fig. 2(c1)). These phenomena could be due to the worse solubility of EPE 3500 in water. Specially, as listed in Table I, there was only 10 wt% hydrophilic EO segment in EPE 3500 molecules. Furthermore, its molecular weight was higher than EPE 1000 and EPE 2000. These were possible reasons for the poor solubility of EPE 3500 in water. In the copper plating bath, when the concentration of EPE 3500 was high (e.g., 200 ppm), the molecules were able to assemble and form large micelles with a structure of PO core and EO shell in order to minimize the free energy of the system. In addition, the size of micelles formed from EPE 3500 should be larger than those from EPE 1000 or EPE 2000 as evidenced by the fact that only the plating bath containing 200 ppm EPE 3500 was thick and semitransparent. As a result, only large micelles can adsorb on the sample, leading to a poor microvia filling.

Compared with EPE 3500, EPE 2450 contained more EO segments and had a lower molecular weight. Thus, the solubility of EPE 2450 should be better than EPE 3500 and probably resulted in better filled microvias as exhibited in Fig. 2(d2). However, a lot of small pits on the surface of the deposited copper film and the big cavity near the mouth of the microvia can be observed in Fig. 2, likely due to the relatively insufficient solubility of EPE 2450 compared to EPE 2900.

According to the literature,<sup>21,29</sup> increasing PO segments in the molecule can strengthen the suppression and improve filling performance of the plating bath. On the other hand, excess PO segments in the molecule also lead to a lower solubility of the triblock copolymer in water, which was unfavorable to the filling performance. Overall, suppression strength and solubility were found to be two key factors to the filling performance of the plating bath when triblock copolymers were used for suppressors and it was easy to understand why the plating bath with EPE 2900 showed better filling performance than that with EPE 2450 and EPE 8000.

As displayed in Fig. 2(g2), superfilling occurred in the microvia when PEG 6000 was used as the suppressor. However, the microvia was not fully filled. According to the cross-sectional views of the microvias in Fig. 2, it could be concluded that the order of filling performances measured with these studied triblock copolymer was: EPE 2900 > EPE 2450 > EPE 2000 > EPE 1000 > EPE 8000 > PEG 6000 > EPE3500.

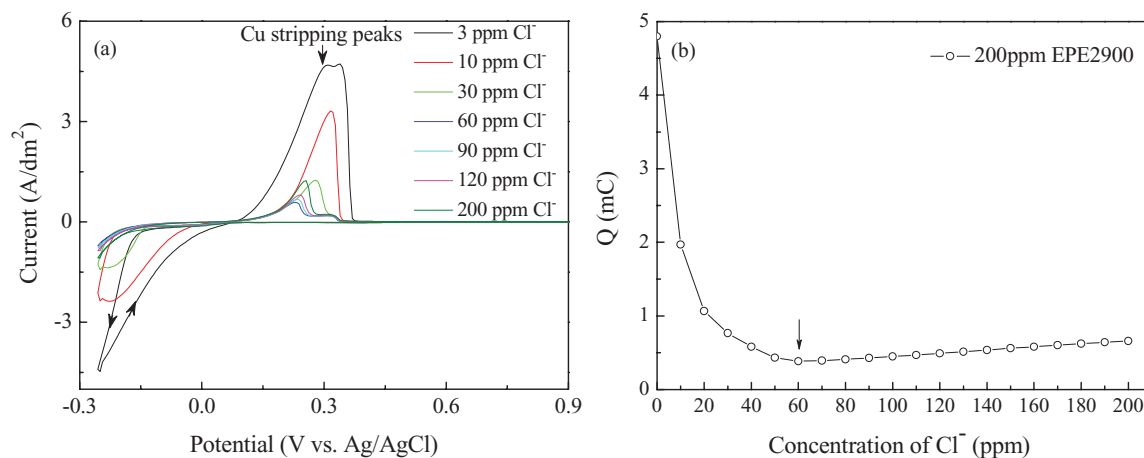
Using galvanostatic technique, the potential-time curves were recorded for each triblock copolymer suppressor, as shown in Fig. 3. The potential difference ( $\Delta\eta$ ) of each suppressor at 100 and 1000 rpm rotation speeds was compared in Table II. The sequence of these  $\Delta\eta$  values was: EPE 2900 > EPE 2450 > EPE 2000 > EPE 1000 > EPE 8000 > PEG 6000 > EPE3500. Importantly, this order was in good agreement with that of the filling performance.

*Filling performances of triblock copolymer suppressors at a low concentration (20 ppm) with the optimal  $\text{Cl}^-$  concentration.*— Due to the superior performance of EPE 2900 in the typical copper plating formula, further investigation was carried out using CV measurements to determine the optimal  $\text{Cl}^-$  concentration for 200 ppm EPE 2900 (Fig. 4a). When  $\text{Cl}^-$  concentration was increased from 3 to 200 ppm, the areas of copper stripping peaks first decreased and then increased, as evidenced by the charge of Cu stripping peak ( $Q$ ) as a function of  $\text{Cl}^-$  concentration (Fig. 4b). Furthermore, the onset potential of copper deposition first shifted negatively and then positively, suggesting that the suppression strength of EPE 2900 first increased and then decreased. After the addition of 60 ppm  $\text{Cl}^-$  into the electrolyte, the suppression strength of EPE 2900 reached the maximum.

As discussed above, EPE 3500 and EPE 2450 with a high concentration such as 200 ppm showed worse performance because of their lower solubility in water. In order to compare these suppressors more reasonably, it was necessary to reduce the concentration of the suppressor for other less soluble copolymers (e.g. EPE 3500, EPE 2450) in the plating bath as well as to find out the optimal  $\text{Cl}^-$  concentration for them. As revealed in Fig. 5, the optimal  $\text{Cl}^-$  concentration for each suppressor at a concentration of 20 ppm was determined using CV measurements, which was marked with the upward arrow. It can be seen obviously from Fig. 5a that the optimal  $\text{Cl}^-$  concentrations for EPE 1000, EPE 2000, and EPE 3500 were 65, 40, and 25 ppm,

**Table II.** Potential differences of the suppressors calculated from GMs shown in Fig. 3.

Suppressors (200 ppm)	The first group			The second group			
	EPE 1000	EPE 2000	EPE 3500	EPE 2450	EPE 2900	EPE 8000	PEG 6000
Potential Differences $\Delta\eta$ (mV)	16.2	17.7	12.8	19.7	22.1	14.3	15.3



**Figure 4.** (a) CV curves obtained in the electrolyte (220 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 55 g/L  $\text{H}_2\text{SO}_4$ ) with 200 ppm EPE 2900 and different amounts of  $\text{Cl}^-$ ; (b) the corresponding Q value as a function of  $\text{Cl}^-$  concentrations. Here Q is the integral value of the Cu stripping peak.

respectively. Because the ratios of EO segments in EPE 1000, EPE 2000, and EPE 3500 are the same, it could be described that the optimal  $\text{Cl}^-$  concentration decreased significantly as an increase of the molecular weight. Moreover, it was obvious that the relationship of Q values obtained in the electrolyte with different suppressors was: EPE 1000 < EPE 2000 < EPE 3500. This result suggested that EPE 1000 exhibited the strongest suppression strength for Cu deposition.

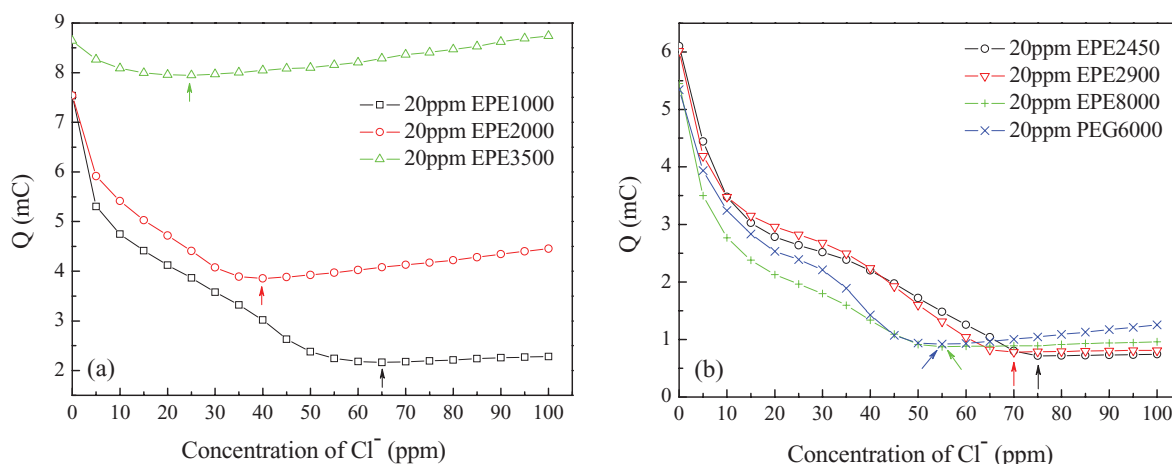
As shown in Fig. 5b, the optimal  $\text{Cl}^-$  concentrations for EPE 2450, EPE 2900, EPE 8000, and PEG 6000 were 75, 70, 55, and 55 ppm, respectively. Because EO ratios and molecular weights as two variables simultaneously were changed, it was difficult to assign the differences of the optimal  $\text{Cl}^-$  concentrations unequivocally to either one. However, it could be clearly observed that the differences between the optimal  $\text{Cl}^-$  concentrations of these suppressors were insignificant, which might be mainly governed by the higher EO fractions in these suppressors.

Using the optimal  $\text{Cl}^-$  concentration in the electrolyte, the suppression strengths of different suppressors were investigated by LSV method as highlighted in Fig. 6. In the first group, the order of suppression strengths of the suppressors was EPE 1000 > EPE 2000 > EPE 3500 at a current density of 2 A/dm<sup>2</sup>, as shown in Fig. 6a. This observation was in good agreement with that obtained from Fig. 5a that EPE 1000 exhibited the smallest Q value for Cu deposition. In addition, it could be seen that the electrolyte with EPE 3500 exhibited the smallest and steadiest current density until the potential

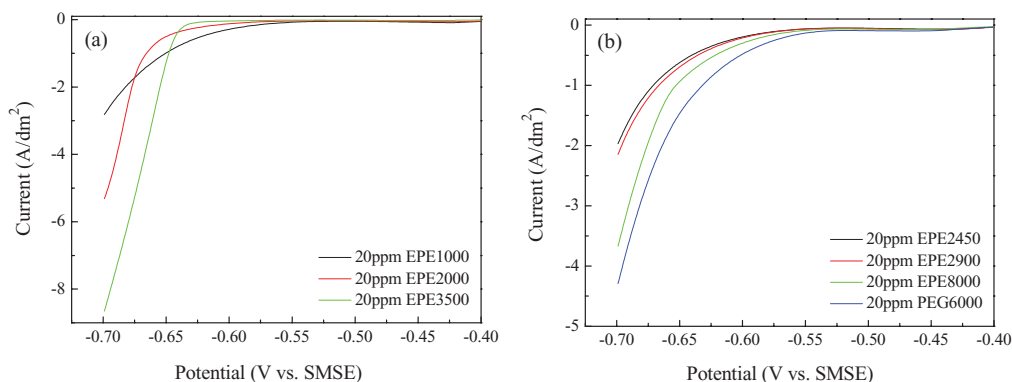
was negatively shifted to about  $-0.64$  V vs. SMSE. After that, the current density was increased sharply. In addition, the curve obtained in the electrolyte with EPE 2000 was similar to that with EPE 3500. The only difference was that the onset potential of copper deposition was shifted negatively. Compared to EPE 2000 and EPE 3500, the increase of current density measured in the electrolyte with EPE 1000 started at  $-0.57$  V vs. SMSE followed by a slow increment. All the above results obtained from Fig. 6a indicated that EPE 3500 had the strongest suppression strength until the potential was negative enough for its desorption from the Cu-RDE. Moreover, the desorption process of EPE 3500 was found quickly on the cathode during the negative-going sweep, while EPE 1000 showed the slowest desorption process among these three suppressors. It demonstrated that the potential range for EPE 1000 desorbed from the cathode surface was broader than that of EPE 2000 or EPE 3500. This may due to their difference in molecular weight.

With regard to the second group of triblock copolymers, the LSV curves measured in the electrolyte with different suppressors were very similar, especially for EPE 2450 and EPE 2900. The order of suppression strengths of the suppressors was: EPE 2450 > EPE 2900 > EPE 8000 > PEG 6000. That meant the more PO segments in the molecules would lead to the stronger suppression strength of the suppressors. This result was in line with that observed by West et al.<sup>21</sup>

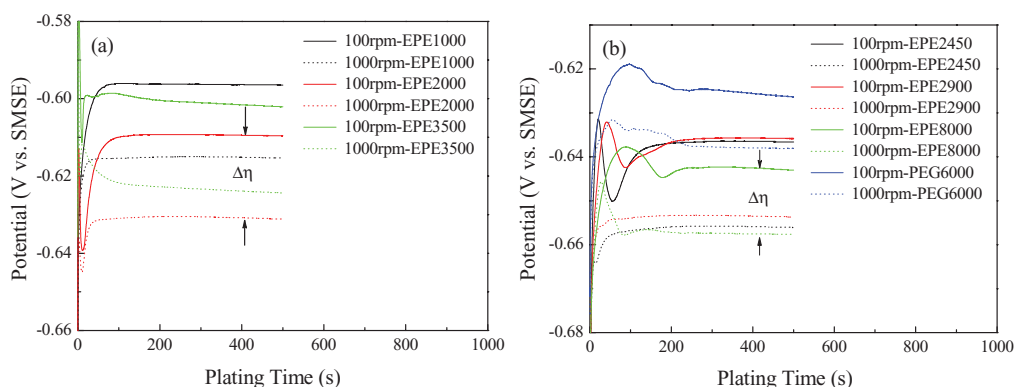
Using the optimized  $\text{Cl}^-$  concentrations for each suppressor, GMs were performed for evaluating the filling performances of the plating



**Figure 5.** CV measurement of Q value as a function of  $\text{Cl}^-$  concentration in the electrolyte (220 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 55 g/L  $\text{H}_2\text{SO}_4$ ) with 20 ppm suppressor: (a) the first group of suppressors; (b) the second group of suppressors.



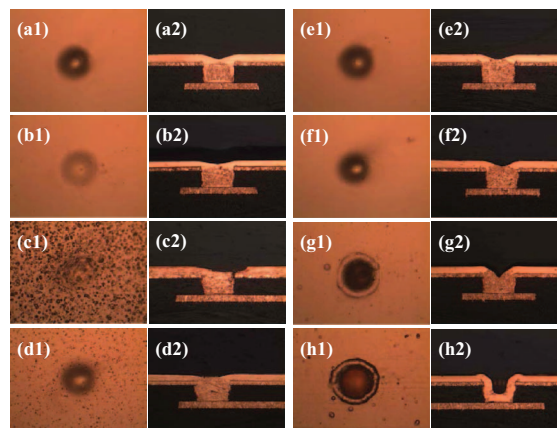
**Figure 6.** The current-potential curves measured by LSV in the electrolyte (220 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 55 g/L  $\text{H}_2\text{SO}_4$ ) with 20 ppm suppressor and the corresponding optimal  $\text{Cl}^-$  concentration: (a) the first group of suppressors; (b) the second group of suppressors.



**Figure 7.** GMs performed in the plating baths using different suppressors and their corresponding optimal  $\text{Cl}^-$  concentration at two different rotation speeds: (a) the first group of suppressors; (b) the second group of suppressors. The plating bath is composed of 220 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 55 g/L  $\text{H}_2\text{SO}_4$ , 3 ppm SPS, 4 ppm JGB and 20 ppm suppressor.

baths containing suppressors at a low concentration of 20 ppm suppressors, as shown in Fig. 7. The corresponding potential differences ( $\Delta\eta$ ) for the suppressors at different rotation speeds were compared in Table III. The  $\Delta\eta$  values in the first group were increased in the order of EPE 1000 < EPE 2000 < EPE 3500. In the second group, the order was EPE 2450 > EPE 2900 > EPE 8000 > PEG 6000. Importantly, in the second group, the stronger suppression strength corresponded to the better filling performance of the plating bath. This conclusion was consistent with that demonstrated by West et al.<sup>20</sup> On the contrary, in the first group, the stronger suppression strength of the suppressor would result in the worse filling performance of the plating bath, which may be caused by the different desorption behavior of these suppressors.

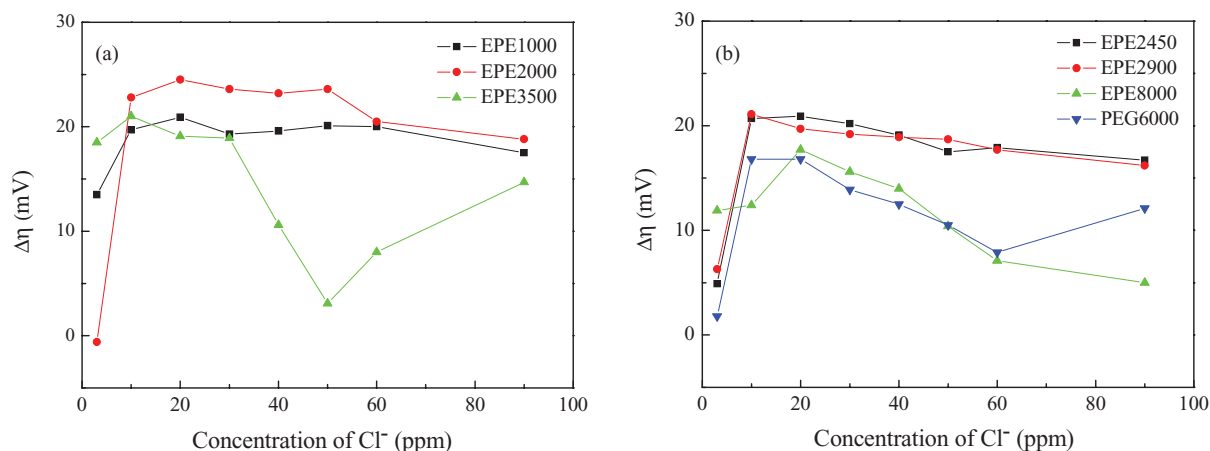
In order to verify the reliability of GMs for evaluating the filling performance, real filling experiments were carried out at a current density of 2 A/dm<sup>2</sup> for 100 min. Fig. 8 indicated that all microvias were filled by deposited copper in a mode of superfilling except for PEG 6000 as the suppressor. Moreover, the microvias were almost fully filled in the plating baths using EPE 1000, EPE 2000, EPE 3500, EPE 2450, or EPE 2900 as the suppressors. Specially, the microvia obtained in the plating bath with EPE 2000 showed a smaller dimple as well as a bright surface. Unexpectedly, EPE 3500 with the largest  $\Delta\eta$  value showed a worse performance. As shown in Fig. 8(c1), there were a lot of small pits on the deposited copper surface. In addition,



**Figure 8.** Optical microscope images of microvias after electroplated in different plating baths. The plating bath is composed of 220 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 55 g/L  $\text{H}_2\text{SO}_4$ , 60 ppm  $\text{Cl}^-$ , 3 ppm SPS, 4 ppm JGB and a low concentration of suppressor. The suppressors are: (a) 20 ppm EPE 1000, (b) 20 ppm EPE 2000, (c) 20 ppm EPE 3500, (d) 10 ppm EPE 3500, (e) 20 ppm EPE 2450, (f) 20 ppm EPE 2900, (g) 20 ppm EPE 8000, and (h) 20 ppm PEG 6000. 1 and 2 correspond to top views and cross-sectional views, respectively. All the images are magnified 200 $\times$ .

**Table III.** Potential differences of the suppressors calculated from GMs shown in Fig. 7.

Suppressors (20 ppm)	The first group			The second group			
	EPE 1000	EPE 2000	EPE 3500	EPE 2450	EPE 2900	EPE 8000	PEG 6000
Potential Differences $\Delta\eta$ (mV)	18.1	20.0	21.7	18.1	16.3	13.7	11.8



**Figure 9.** Relationship between  $\Delta\eta$  value and  $\text{Cl}^-$  concentration. The  $\Delta\eta$  values were obtained from GMs which were performed in the plating bath for 1000 s using different suppressors at a wide operation window of  $\text{Cl}^-$ . The plating bath is composed of 220 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 55 g/L  $\text{H}_2\text{SO}_4$ , 20 ppm suppressor, 3 ppm SPS, 4 ppm JGB and different  $\text{Cl}^-$  concentrations.

the cross-sectional view shown in Fig. 8(c2) was very similar to that shown in Fig. 2(d2) using 200 ppm suppressors. According to the previous discussion, EPE 3500 had the smallest solubility in water compared to other suppressors, which was most likely the reason for its worse performance in microvia filling process. This conclusion was supported by Fig. 8(d1) and 8(d2) which were obtained in the plating bath with a lower concentration of 10 ppm EPE 3500.

*GMs to evaluate the filling performance of triblock copolymer suppressors at a wide operation window of  $\text{Cl}^-$ .*— According to the discussion above, it was known that, with the increase of  $\text{Cl}^-$  concentration, the suppression strength of the suppressors first increased and then decreased. Each suppressor showed the strongest suppression strength at the optimal  $\text{Cl}^-$  concentration. With the optimal  $\text{Cl}^-$  concentrations, the filling performances of the plating baths using these suppressors were compared. This comparison only focused on the influence of  $\text{Cl}^-$  on the suppression strength of the suppressors. In consideration of the influence of  $\text{Cl}^-$  concentration on SPS and JGB, GMs were carried out in the plating bath using different suppressors at a wide operation window of  $\text{Cl}^-$  respectively. The corresponding  $\Delta\eta$  value as a function of  $\text{Cl}^-$  concentration was shown in Fig. 9. It can be seen from Fig. 9a that the  $\Delta\eta$  values obtained in the plating bath using EPE 2000 as the suppressor were always larger than that with EPE 1000 or EPE 3500 regardless the  $\text{Cl}^-$  concentration increasing from 10 to 90 ppm. It indicated that the filling performance based on EPE 2000 was better than EPE 1000 or EPE 3500 at the wide operation window of  $\text{Cl}^-$ . In the second group, EPE 2900 and EPE 2450 showed the similar performances which were much better than EPE 8000 and PEG 6000, as shown in Fig. 9b.

### Conclusions

Ethylene-propylene-ethylene (EPE) oxide triblock copolymers were systematically studied in terms of their application as suppressors for microvia filling by copper electroplating. Using a typical copper electroplating formula with 200 ppm suppressor and 60 ppm  $\text{Cl}^-$ , EPE 2900 as the suppressor showed the best filling performance compared to other studied triblock copolymers. As for the alcohol-soluble copolymers defined as the first group (EPE 1000, EPE 2000, and EPE 3500), the optimal  $\text{Cl}^-$  concentration decreased obviously with an increase of the molecular weight. Furthermore, the stronger suppression strength of the suppressor from the first group would result in the worse filling performance of the corresponding plating bath, as evidenced by the electrochemical measurements and cross-sectional views. However, an opposite trend was obtained in the water-soluble copolymers (EPE 2450, EPE 2900, and EPE 8000), defined as the sec-

ond group. Comparing all the cross-sectional views of the microvias after electroplated in the plating bath with the high (200 ppm) or low concentration (20 ppm) of suppressor, it could be obtained that EPE 2000 in the first group and EPE 2900 in the second group had the best performance in microvia filling. This result was in good agreement with that of galvanostatic measurements performed at a broad range of  $\text{Cl}^-$  concentration from 3 to 90 ppm. Importantly, the galvanostatic measurements and linear sweep voltammetry were found effective to electrochemically study the microvia filling performance of additives such as suppressors and accelerators.

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