An effective triblock copolymer as a suppressor for microvia filling via copper electroplating

Ning Xiao a, Deyu Li a, Guofeng Cui b, Ning Li a,*, Dong Tian a, Qing Li c, Gang Wu c,**

a Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, China
b School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China
c Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

A R T I C L E   I N F O
Article history:
Received 14 April 2013
Received in revised form 16 July 2013
Accepted 16 July 2013
Available online xxx

Keywords:
Microvia filling
Copper electroplating
Suppressor
Triblock copolymer
Adsorbing mechanism

A B S T R A C T
In this work, an effective suppressor was found in copper electroplating solution for microvia filling. The suppressor is a triblock copolymer comprised of ethylene oxide (EO)—propylene oxide (PO)—ethylene oxide (EO) with a molecular weight of 2900 (EPE 2900). In terms of the obtained filling performance evaluated by observing the obtained cross-sectional views of the microvias after electroplating, the electroplating solution was systematically studied as functions of Cl− concentration, EPE 2900 concentration, and convection conditions. It was found that filling performance was greatly dependent on these key factors. In the developed copper electroplating formulation, EPE 2900 was able to yield sufficient filling performance in a broad Cl− concentration ranging from 3 to 200 ppm, although the optimized value was determined to be about 30 ppm in terms of the best filling performance. During the microvia filling process, Cl− concentration, EPE 2900 concentration, and forced convection would affect each other. Their interactions were studied based on the anchor effect of Cl− on the adsorption of EPE 2900 on Cu substrates. In doing so, extensive electrochemical experiments including galvanostatic measurements, linear sweep voltammetry, electrochemical impedance spectroscopy and cyclic voltammetry were employed to study the adsorption behavior of EPE 2900 on the cathode during both the copper electrodeposition and dissolution processes. An adsorbing mechanism of EPE 2900 on cathode was proposed to elucidate the promotional role in improving the microvia filling performance.

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1. Introduction

In electronic industry, microvia filling via copper electroplating can be used to connect the adjacent two or more layers of the printed circuit board (PCB). In order to achieve the reliable electrical interconnection, the microvia should be fully filled by depositing copper without seam or void in an acid copper plating solution containing different key additives [1–8]. As reported before, “superfilling” or “bottom-up filling” can be realized by using polyethylene glycol (PEG) as suppressor, such as PEG–CI, PEG–SPS–CI, PEG–MPS–CI, PEG–SPS–Cl–JGB, etc. [9–18]. However, a new class of suppressor using triblock copolymers (EPE) of ethylene oxide (EO)—propylene oxide (PO)—ethylene oxide (EO) for microvia filling is not extensively reported yet [19–21].

In our previous reports [22,23], it was demonstrated that there is an obvious synergistic effect between EPE 2900 (an EPE triblock copolymer with a molecular weight of 2900) and Cl− on inhibiting copper deposition during the microvia filling process. Given a fixed EPE 2900 concentration, there existed an optimal Cl− concentration to achieve the maximum synergistic effect. The suppression strength and microvia filling performance obtained from such type of triblock copolymers of EO–PO–EO with various molecular weight and EO content were systematically compared [23]. Among the studied triblock copolymers, the EPE 2900 exhibited the strongest suppression strength on inhibiting copper deposition, showing the best performance during the microvia filling. However, the adsorption behavior of EPE 2900 on the cathode was not elucidated yet. Further understanding its inhibiting mechanism will be greatly helpful to guide the selection of suppressor in microvia filling via copper electroplating.

In this work, microvia filling performance of the copper plating solution using EPE 2900 as a suppressor is investigated by means of extensive electrochemical methods. It has been found that the EPE 2900 can form micelles with a hydrophilic shell (PEO segments) and a hydrophobic core (PPO segments) in aqueous solution [24,25]. The correlations between obtained filling performance and studied solution formulations indicate that the copper plating solution...
containing the EPE 2900 with an optimal concentration (200 ppm) is able to offer sufficient filling performance in a wide operation window of Cl\(^-\). Specially, with the assistance of forced convection, superfilling can be fully achieved in the plating solution containing Cl\(^-\) as low as 3 ppm. Interestingly, when Cl\(^-\) concentration is increased to 30 ppm, the role of EPE 2900 is overwhelmed by Cl\(^-\), and further increasing the triblock copolymer concentration shows insignificant influence on the filling performance. A series of electrochemical experiments are carried out to study the adsorption behavior of the EPE 2900 on the cathode during the copper electrodeposition, with an aim to establish the correlations between the microvia filling performance and the concentration of EPE 2900 and Cl\(^-\).

2. Experimental

2.1. Microvia filling via copper electroplating

PCBs with microvias fabricated by CO\(_2\) laser ablation were used as testing samples for the microvia filling experiments. The dimension of the PCB sample was 5 × 12 cm\(^2\) with an effective area of 5 × 9 cm\(^2\). The diameter and depth of the microvia were 150 μm and 75 μm, respectively. Prior to microvia filling, the sidewalls of these microvias were metallized by electroless copper plating to deposit a 2–3 μm copper film. In these experiments, phosphorus-containing (0.03–0.065 wt%) copper plates with a size of 6 × 12 cm\(^2\) were used as anodes and directly placed in the plating bath containing 1.5 L solution. The current density for copper plating was controlled at 2 A/dm\(^2\) and the electroplating time was 100 min. Unless otherwise specified, forced convection by continuously bubbling air flow in the solution was applied during these microvia filling experiments so as to ensure efficient mass transfer.

The electroplating solution used for microvia filling experiments was composed of 220 g/L CuSO\(_4\)·5H\(_2\)O, 55 g/L H\(_2\)SO\(_4\), 3 ppm bis(3-sulfopropyl) disulfide (SPS), 4 ppm Janus Green B (JGB) as well as Cl\(^-\) (added as NaCl), EPE 2900 with varying concentration. EPE 2900 (BASF) was a triblock copolymer with the structure of EO–PO–EO. It has a nominal molecular weight of 2900 and contains approximately 40 wt% EO. Temperature of the plating solution was controlled at 25 \(^\circ\)C. The filling performance of the plating bath was evaluated by cross-sectional views of the microvias using optical microscopy (DFC290, Leica) at a magnification of 200×.

2.2. Electrochemical measurements

Galvanostatic measurements (GMs), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (CHI 760D) in a three-electrode cell at 25 °C. A platinum rotating disk electrode (Pt-RDE, Pine) with a diameter of 5 mm and a small piece of copper bar were employed as the working electrode and counter electrode, respectively. A saturated mercury–mercurous sulfate electrode (MSE) was used as the reference electrode. Prior to electrochemical measurements, 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 conducted at a constant current density of 2 A/dm\(^2\) and at different rotating speeds of 100, 400, and 1000 rpm. According to the reported literatures [11,26], Δη values, which corresponded to an averaged potential difference measured at a rotating speeds of 100 and 1000 rpm, can be used as indicators of the filling performance when forced convection was applied in the plating bath. Larger Δη values usually suggest better filling performance. In the meantime, the Δη value between 100 rpm and 400 rpm was calculated to evaluate the filling performance of the plating solution without forced convection.

The LSV polarization plots were recorded with a negative-going sweep from open circuit potential to −0.7 V vs. MSE at a scan rate of 1 mV/s. EIS measurements were performed at −0.65 V vs. MSE. The frequency range was from 100 K to 0.1 Hz with an amplitude of 5 mV. The impedance data were fitted using equivalent circuit by using ZSimpWin software. The rotating speed of the Cu-RDE was held at 1000 rpm during the LSV and EIS measurements.

Cyclic voltammetry (CV) was carried out using a Pt/Pt rotating ring-disk electrode (RRDE) as the working electrode (Pt disk radius \(r_1 = 4.57 \, \text{mm}\); Pt ring inner radius \(r_2 = 4.93 \, \text{mm}\) and outer radius \(r_3 = 5.38 \, \text{mm}\)). The Pt/Pt RRDE was mechanically polished with alumina powders before each measurement. The counter electrode was a Pt plate with an area of 1 cm\(^2\) and the reference electrode was MSE. The potential of the disk was negatively swept from 1.0 V to −0.6 V and then back to 1.0 V vs. MSE with a scan rate of 5 mV/s. In the meantime, the ring potential was kept at 0.2 V vs. MSE which was positive enough to oxidize the Cu\(^+\) to Cu\(^{2+}\) at the ring electrode. The rotation speed of the RRDE was 1000 rpm during the CV measurements.

Unless otherwise specified, electrolyte used for all of the electrochemical measurements was composed of 220 g/L CuSO\(_4\)·5H\(_2\)O,

![Fig. 1](image-url) (a1–a6) Cross-sectional views of microvias after electroplating in the plating solution containing 200 ppm EPE 2900 and different Cl\(^-\) concentration.
55 g/L H₂SO₄, 3 ppm SPS, 4 ppm JGB, Cl⁻ and EPE 2900, in which the concentration of EPE 2900 and Cl⁻ was specified in each experiment.

3. Results and discussion

3.1. Role of Cl⁻ in microvia filling

The cross-sectional views of the microvias and the corresponding GMs as a function of Cl⁻ concentration are shown in Figs. 1 and 2, respectively. Without adding any Cl⁻ in the plating solution, conformal deposition is observed in the microvia (Fig. 1(a)), which is detrimental to PCB fabrication. As displayed in Fig. 2, the potential obtained at 1000 rpm is more negative than that obtained at 100 rpm with a Δη value of −10.1 mV listed in Table 1. According to the galvanostat method proposed by Dow et al. [11, 27], the negative Δη value implies that no superfilling can occur in the microvia, which is in good agreement with our observed microvia filling results. After 3 ppm Cl⁻ is added into the plating bath, bottom-up deposition appears and the microvias are almost fully filled by deposited copper. Only a small dimple is observed near the mouth of the microvia. When the Cl⁻ concentration is further increased up to 200 ppm, the size of the dimple firstly decreases and then increases. As a result, the plating solution yields the best filling performance at a Cl⁻ concentration of 30 ppm. This is in good agreement with the GM results, which the Δη value obtained in the plating solution containing 30 ppm Cl⁻ is the greatest, as listed in Table 1. The obtained results indicate that galvanostat method is effective and reliable to evaluate the microvia filling performance in our experiments.

3.2. Role of EPE 2900 in microvia filling

At a very low Cl⁻ concentration of 3 ppm, the filling performance is greatly dependent on the concentration of EPE 2900, as shown in Fig. 3(a1)–(a4). When EPE 2900 concentration is increased from 10 to 50 ppm, a large dimple near the mouth of the microvia can still be observed. However, upon the concentration reaching 100 ppm, the dimple almost disappears. This phenomenon is due to enhanced suppression strength on copper surface caused by electrostatic adsorption of EPE 2900. Further increasing EPE 2900 concentration to 200 ppm, the dimple in the microvia becomes larger again as shown in Fig. 3(a4), which can be attributed to the insignificant difference of suppression between inside the microvia and on the board surface.

It is worth noting that the filling performance measured with the plating solution containing a high Cl⁻ concentration (30 ppm) becomes less dependent on the EPE 2900 concentration. The microvia can be well filled in the plating solution containing only 10 ppm EPE 2900 (Fig. 3(b1)). Since Cl⁻ is able to serve as anchors for the subsequent adsorption of the suppressor [28], the adsorption of EPE 2900 on the copper surface could be greatly enhanced in the presence of higher Cl⁻ concentration. Thus, the copper surface is totally covered by EPE 2900 even at its relatively low concentration. As a result, an increase of EPE 2900 cannot significantly further improve filling performance, that is, the filling performance seems to be independent of EPE 2900 concentration.

3.3. Role of forced convection in microvia filling

According to the convection-dependent adsorption (CDA) mechanism [28], strong convection can selectively transfer more
Cl\textsuperscript{–} ions to the cathode surface per unit time, thereby facilitating the subsequent adsorption of EPE 2900 in the plating solution. Thus, the deposition rate of copper at outside microvias can be decreased when more Cl\textsuperscript{–} ions are around due to the enhanced convection strength. As displayed in Fig. 4(a), three curves measured with the plating solution correspondingly containing 10, 60, and 200 ppm Cl\textsuperscript{–} attest a great dependence of microvia performance on the strength of forced convection. Hence, the absolute values of the potential gradually increase with the rotating speed varying from 100 to 1000 rpm. This is in good agreement with the proposed CDA mechanism [28].

As a matter of fact, the potential differences between 100 and 400 rpm ($\Delta\eta_{100\text{rpm}-400\text{rpm}}$) and those between 100 and 1000 rpm ($\Delta\eta_{100\text{rpm}-1000\text{rpm}}$) are both positive, which indicates that superfilling can be realized in these plating solutions regardless of whether forced convection is applied or not. However, the curve measured with 3 ppm Cl\textsuperscript{–} is found to be somehow independent of rotating speed ranging from 100 to 400 rpm. The recorded curves are unstable during the measurements, which make it difficult to determine the $\Delta\eta$ values. Thus, GMs was performed in the plating solution containing 3 ppm Cl\textsuperscript{–} at different rotating speeds ranging from 100 to 1000 rpm. As shown in Fig. 4(b), while the $\Delta\eta$ value between 100 and 400 rpm is about 0 mV, this value is increased to 7 mV between 100 and 1000 rpm. This indicates that superfilling cannot effectively occur with the plating solution containing 3 ppm Cl\textsuperscript{–} unless a strong forced convection is applied. In addition, the results obtained from Fig. 4 are in good agreement with the microvia filling experiments exhibited in Fig. 5. Specifically, only is the Cl\textsuperscript{–} concentration higher than 10 ppm, its filling performance becomes independent of forced convection.

### 3.4. Adsorption behavior of EPE 2900

In order to further understand the suppression role of EPE 2900 during the microvia filling process and explain the results shown in Fig. 3, extensive electrochemical measurements are performed in the plating solution with different Cl\textsuperscript{–} and EPE 2900 concentration to study the adsorption behavior of EPE 2900.

In these experiments, the plating solution containing 10 ppm EPE 2900 and 3 ppm Cl\textsuperscript{–} is used as a base formula, further addition of EPE 2900 or Cl\textsuperscript{–} is carried out to study their influences on copper electrodeposition. As shown in Fig. 6, increased overpotential of copper deposition can be observed at a current density...
of 2 A/dm². In other words, with the increase of EPE 2900 or Cl⁻ concentration, the suppression strength of EPE 2900 toward copper deposition is enhanced. It suggests that there should be more EPE 2900 molecules adsorbed onto the cathode surface. Due to the blockage resulted from adsorption of EPE 2900, the Cu²⁺ ions in the plating solution become more difficult to diffuse to the cathode surface. In addition, the active sites for copper deposition on the cathode surface are decreased due to a large number of adsorbed EPE 2900 molecules.

It should be noted that, compared to the EPE 2900, variation of Cl⁻ concentration exhibit more significant effect on the overpotential of copper electrodeposition. This phenomenon is due to the different adsorption behavior of EPE 2900 in the presence or absence of Cl⁻. It is very likely that EPE 2900 is able to complex with Cu²⁺ and Cl⁻ to form EPE 2900–Cu²⁺–Cl⁻, which is similar to PEG–Cu²⁺–Cl⁻. Because EPE 2900 and PEG are both polyethers and contain the same structure units of EO, this complex can replace water molecules and strongly adsorb onto the inner Helmholtz layer of the cathode to inhibit copper deposition. In contrast, most EPE 2900 molecules only weakly adsorb onto the outer Helmholtz layer of the electrode via electrostatic and Van der Waals force when Cl⁻ is absent or insufficient.

As shown in Fig. 7, the stable potential of copper electrodeposition shifts negatively when the concentration of either EPE 2900 or Cl⁻ increases. In particular, the increase of Cl⁻ shows more significant influence on the stable potential compared to EPE 2900. All these results are consistent with LSV measurements.

In order to provide insights into the adsorption behavior of EPE 2900 as a function of Cl⁻ concentration, EIS measurements are employed to study the copper deposition. The Nyquist plots recorded at −0.65 V vs. MSE for different plating solution are compared in Fig. 8(a). The corresponding equivalent circuit is presented in Fig. 8(b). It can be seen that the simulated plots represented by solid lines are well fit with the experimental ones. According to the literatures [29–31], in the equivalent circuit, \( R_s \) represents the resistance of the solution. The double layer capacity of CPE₁ in parallel to the charge transfer resistance of \( R_1 \) is related to the capacitive loop in the high frequency. CPE₂ in parallel to \( R_2 \) corresponding to the second capacitive loop are caused by the relaxation process of (Cuads⁺). \( L \) corresponding to the inductive loop is resulted from the relaxation process of Cu²⁺–SPS. It is well known that the electrodeposition of copper usually includes two steps: Cu²⁺ + e⁻ → Cu⁺ (step 1) and Cu⁺ + e⁻ → Cu (step 2). Among them, step 1 is a kinetically slow reaction and is considered to be the rate-determining step. In the employed equivalent circuit, the size of \( R_1 \) is used to evaluate the

![Fig. 6](image.png)  
Fig. 6. The current–potential curves measured by LSV in the plating solution containing different EPE 2900 and Cl⁻ concentration: (a) 0 ppm EPE 2900 and 3 ppm Cl⁻; (b) 10 ppm EPE 2900 and 3 ppm Cl⁻; (c) 100 ppm EPE 2900 and 3 ppm Cl⁻; (d) 10 ppm EPE 2900 and 30 ppm Cl⁻; (e) 100 ppm EPE 2900 and 30 ppm Cl⁻.

![Fig. 7](image.png)  
Fig. 7. GMs performed in the plating solution containing different EPE 2900 and Cl⁻ concentration.

![Fig. 8](image.png)  
Fig. 8. (a) Nyquist plots recorded from the plating solution containing different EPE 2900 and Cl⁻ concentrations. Point: tested data, solid line: fitted curve. (b) Equivalent circuit of EIS.

<table>
<thead>
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<th>Additive concentration</th>
<th>( R_1/Ω \text{ cm}^2 )</th>
<th>( R_1/Ω \text{ cm}^2 )</th>
<th>( R_2/Ω \text{ cm}^2 )</th>
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<tr>
<td>10 ppm EPE 2900 + 3 ppm Cl⁻</td>
<td>5.4</td>
<td>66.7</td>
<td>0.1</td>
</tr>
<tr>
<td>100 ppm EPE 2900 + 3 ppm Cl⁻</td>
<td>5.0</td>
<td>79.2</td>
<td>1.8</td>
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<tr>
<td>10 ppm EPE 2900 + 30 ppm Cl⁻</td>
<td>5.0</td>
<td>129.4</td>
<td>19.3</td>
</tr>
<tr>
<td>100 ppm EPE 2900 + 30 ppm Cl⁻</td>
<td>4.8</td>
<td>227.2</td>
<td>21.3</td>
</tr>
</tbody>
</table>

Table 2: Simulated impedance parameters as functions of EPE 2900 and Cl⁻ concentration.
The concentration of Cl\(^{-}\) in the plating solution containing different EPE 2900 and Cl\(^{-}\), concentration: (a) 10 ppm EPE 2900 and 3 ppm Cl\(^{-}\); (b) 100 ppm EPE 2900 and 3 ppm Cl\(^{-}\); (c) 10 ppm EPE 2900 and 30 ppm Cl\(^{-}\); (d) 100 ppm EPE 2900 and 30 ppm Cl\(^{-}\).

The suppression strength of EPE 2900 and Cl\(^{-}\) on inhibiting copper deposition.

As listed in Table 2, the corresponding R\(_1\) values are increased from 66.7 to 79.2 \(\Omega\) cm\(^2\) when EPE 2900 concentration increases from 10 to 100 ppm at a constant Cl\(^{-}\) concentration of 3 ppm. Upon fixing the EPE 2900 concentration at 10 ppm, increasing Cl\(^{-}\) concentration from 3 to 30 ppm leads to an increase of R\(_1\) values from 66.7 to 129.4 \(\Omega\) cm\(^2\). Obviously, the rise either in EPE 2900 or Cl\(^{-}\) concentration can enhance the suppression strength of EPE 2900 for inhibiting copper deposition. It is worth noting that enhancement of the suppression strength caused by Cl\(^{-}\) is more significant than that caused by EPE 2900, thereby attesting that adsorption behavior of EPE 2900 is changed due to the presence of Cl\(^{-}\).

In order to provide more insights into the mechanism of copper deposition and obtain direct evidences of EPE 2900 for inhibiting copper deposition, rotating ring-disc electrode is employed to study the possible intermediate, Cu\(^+\), during both copper deposition and copper stripping processes. As shown in Fig. 9, in the plating solution containing 10 ppm EPE 2900 and 3 ppm Cl\(^{-}\), copper is deposited on the Pt disk at potentials below −0.4 V vs. MSE. The reverse scan of the voltammogram shows an anodic stripping peak at −0.24 V vs. MSE due to copper dissolution. Further addition of EPE 2900 or Cl\(^{-}\) leads to negative shifts of deposition potentials. At the same time, the copper stripping peaks become smaller. All these results indicate that copper deposition becomes more difficult on the disk with larger overpotentials, which is consistent with the LSV, GMs and EIS results discussed above.

At the ring electrode, Cu\(^+\), the intermediate during the copper deposition, can be detected by re-oxidizing it to Cu\(^{2+}\). It can be seen from Fig. 9 that the oxidation of Cu\(^{2+}\) is observed at −0.42 V vs. MSE. However, no Cu\(^{+}\) ion is detected at the ring electrode at more negative potentials, where all of Cu\(^{+}\) ions should be reduced to Cu at the disk electrode. During copper dissolution process, the peak of Cu\(^{+}\) is detected again at the ring since it is also an intermediate during the copper dissolution process. It can be seen from Fig. 9 that the peak of Cu\(^{+}\) detected at the ring becomes smaller after either EPE 2900 or Cl\(^{-}\) is added into the plating solution. This suggests that EPE 2900 or Cl\(^{-}\) can effectively prevent the Cu\(^{+}\) escaping from the disk to ring electrode. Considering the depolarization effect of Cl\(^{-}\) on copper deposition process, the most reasonable reason is that the addition of EPE 2900 or Cl\(^{-}\) can lead to formation of EPE 2900–Cu\(^{+}\)–Cl\(^{-}\) that can be strongly adsorbed onto the cathode. As a result, the Cu\(^{+}\) generated on the disk cannot be easily escaped and then detected by the ring electrode. These results are also in good agreement with the EIS data.

In order to study the possible interaction between EPE 2900 and Cu\(^{+}\), CV measurements are performed in the electrolytes containing various EPE 2900 and Cl\(^{-}\) concentration. By using Pt/Pt RRDE, the CV plots are shown in Fig. 10, in accordance with those presented in our previous work [22]. On the ring electrode, solely introducing Cl\(^{-}\) into the electrolyte can increase the Cu\(^{+}\) peak during copper deposition. This can be attributed to the depolarization effect of Cl\(^{-}\), which can accelerate the rate determining step (Cu\(^{2+}\) + e\(^-\) → Cu\(^{+}\)) during the copper deposition [33,34]. On the contrary, the Cu\(^{+}\) peak during the copper deposition almost disappeared after exclusively adding EPE 2900, without Cl\(^{-}\). The reasonable explanation is that EPE 2900 adsorbed onto the disk electrode can react with the intermediate Cu\(^{+}\) to form an EPE 2900–Cu\(^{+}\) complex. Interestingly, the Cu\(^{+}\) peak during the copper dissolution process is greatly increased as shown in Fig. 10(c), which is probably due to the formation of EPE 2900–Cu\(^{+}\) complex. Compared to Cu\(^{+}\), this complex is relatively stable and can exist in the electrolyte for a longer time, but it can no longer adsorb onto the disk electrode due to its positive charge during the copper dissolution process. In the electrolyte simultaneously containing EPE 2900 and Cl\(^{-}\), the Cu\(^{+}\) peak detected during copper deposition process cannot be as obvious as observed before. The corresponding peak potentials shift negatively during dissolution process due to a trend of formation of the Cu\(^{+}\) complex. On the disk electrode, the overpotential for copper deposition is greatly increased, and thus the corresponding copper stripping peak decreases obviously. This is also due to the formation of EPE 2900–Cu\(^{+}\)–Cl\(^{-}\) complex, strongly blocking the copper deposition. Compared to the complex of EPE 2900–Cu\(^{+}\), the EPE 2900–Cu\(^{+}\)–Cl\(^{-}\) is even more stable in the electrolyte and has stronger adsorption strength on the electrode.

4. Conclusions

In this work, a triblock copolymer (EPE 2900) is systematically studied as an effective suppressor in microvia filling via copper electroplating. Both filling performance evaluation and galvanostatic measurements indicate that the copper plating solution containing an optimal EPE 2900 concentration (200 ppm) is able to yield sufficient filling performance in a wide range of Cl\(^{-}\) concentrations. Forced convection applied during the deposition is able to greatly reduce the required Cl\(^{-}\) concentration to 3 ppm, still retaining good microvia filling performance. Likewise, when the
Cl\(^{-}\) concentration increases from 10 to 200 ppm, the filling performance becomes more independent of the applied forced convection. Furthermore, filling performance obtained from the deposition solution containing high Cl\(^{-}\) concentration (above 30 ppm) is also found to be almost independent of EPE 2900 concentration, likely due to the anchoring effect of Cl\(^{-}\) during the adsorption of EPE 2900 to so as to reduce the usage of EPE 2900. These findings can rationally guide to design an effective microvia filling formula with minimum addition of additives. A series of electrochemical measurements are performed to elucidate copper electrodeposition in the microvias in the presence of EPE 2900 and Cl\(^{-}\), which well correlate with the filling performance. This effort can enhance the understanding of the adsorption behavior of EPE 2900 and its interaction with Cl\(^{-}\) and intermediates Cu\(^{2+}\) at the cathode surface. Importantly, in the presence of sufficient Cl\(^{-}\), EPE 2900 can react with Cu\(^{2+}\) and Cl\(^{-}\) to form a stable EPE 2900–Cu\(^{2+}\)–Cl\(^{-}\) complex, capable of strongly adsorbing onto the cathode to inhibit copper deposition. On the contrary, insufficient Cl\(^{-}\) leads to weak adsorption of EPE 2900 on the cathode via electrostatic and Van der Waals force, exhibiting a low suppressing efficiency.

Acknowledgement

This work was financially supported by Hignic Group (China).

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