Adsorption behavior of triblock copolymer suppressors during the copper electrodeposition

Ning Xiao, Deyu Li, Guofeng Cui, Ning Li, Qing Li, Gang Wu

Abstract

Suppressors play a significant role in microvia filling by copper electrodeposition to achieve electrical interconnection of the adjacent layers in printed circuit boards (PCBs). In this work, in order to investigate the adsorption behaviors of one type of triblock copolymer (with a structure of polyethylene oxide - propylene oxide - polyethylene oxide and a molecular weight of 2900, named as EPE2900) on the electrode during the copper electroplating process, electrochemical methods such as cyclic voltammetry (CVS) were employed. The integrated value of the Cu stripping peak was marked as Q, the size of which can reflect the inhibiting strength of EPE2900 on the copper deposition. Then the dependence of Q/Qo values on EPE2900 and Cl− concentrations was studied systematically by the CVS measurements. Here Qo was the integrated value of the Cu stripping peak measured in the base electrolyte. The obtained results indicated that the inhibiting strength of EPE2900 monotonously increased with its concentrations. However, the inhibiting strength of EPE2900 only increased with Cl− concentration when EPE2900 concentration was higher than 20 ppm. Importantly, the critical concentrations of Cl− and EPE2900 in the solution to form an intact barrier layer adsorbing onto the cathode surface were calculated. Based on the results of CVS measurements, a possible adsorption model of EPE2900 was proposed, which was able to reasonably elucidate the CVS measurements. In the meantime, Cu2+–EPE2900–Cl− complexes were formed and very likely involved in the adsorption model, further evidenced by rotating ring-disk electrode (RRDE) techniques.

1. Introduction

Microvia filling though copper electrodeposition is of particular significance to achieve electrical interconnection of adjacent layers in printed circuit boards (PCBs) [1–3]. In order to ensure the safety and reliability, the microvias must be fully filled with deposited copper through electroplating, which is commonly named “superfilling” or “bottom-up deposition” [4–10]. According to the reported literature, superfilling cannot be achieved unless some special additives, such as accelerators and suppressors, are added simultaneously in the electrolyte of Cu deposition [11–15]. In the meantime, a leveler is also vital for obtaining a good microvia filling performance, avoiding the possible overfill bumps formed in the microvias [2,16–18].

To understand the interaction among these additives associated with superfilling, a large variety of microvia or trench filling experiments, electrochemical measurements as well as numerical simulations have been carried out in the past decades [4–6,12,19,20]. As a result, several mechanisms to elucidate the superfilling process have been proposed. One is the curvature-enhanced accelerator coverage (CEAC) model developed by Moffat et al. and West et al. [4,19,20]. In this mechanism, the surface coverage of the accelerator is enhanced when the adsorbed accelerator is concentrated on the ever-decreasing surface area inside of a filling feature to replace larger amounts of suppressor. Another mechanism proposed by Dow et al. is the convection-dependent adsorption (CDA) model [21]. They suggest that strong convection can selectively enhance the suppressing effect of suppressor on the deposition rate of copper by increasing the flux of chloride ions. Superfilling occurs in the microvias due to the differences of convection strength at the bottom and the mouth of the microvias.

Both mechanisms discussed above reveal an important correlation between superfilling and the adsorption behavior of the suppressors during the copper electrodeposition. However, usually several additives simultaneously used in microvia filling include suppressors together with other kinds of functional ones. Those additives are prone to interact with each other during the copper
 electroplating process, which makes it complicated to individually study the properties of the suppressors.

Recently, we have found that there exists a synergistic effect between the triblock copolymer suppressors (e.g., EPE2900) and chloride ions in the copper electroplating solution containing no accelerators or levelers, and its suppressing strength is greatly dependent on the concentration of chloride ions [22]. Furthermore, we have reported that the best microvia filling performance was achieved by using 200 ppm EPE2900 as the suppressor, compared to other studied triblock copolymers [23]. It has been demonstrated that the microvia filling performances are greatly dependent on some key factors, such as Cl− concentration, EPE2900 concentration, and convection conditions [24].

In this work, the adsorption behavior of EPE2900 on the cathode during the copper electrodeposition was systematically investigated by cyclic voltammetric stripping (CVS) in the solution containing only EPE2900 and Cl−. The integrated values of the Cu stripping peak measured in the base solution and the solution containing Cl− and EPE2900 were recorded as Q0 and Q, respectively. The ratio of Q to Q0 was used to evaluate the suppression strength of EPE2900. The Q/Q0 values as functions of Cl− and EPE2900 concentrations were determined, attesting the existence of optimal concentrations for both Cl− and EPE2900. In order to elucidate the measured electrochemical results, a possible model of EPE2900 adsorption on the electrode enhanced by Cl− was proposed. Then, rotating ring-disk electrode (RRDE) techniques were introduced to provide the evidence that Cu+−EPE2900−Cl− complex formed in the proposed adsorption model.

2. Experimental

One series of cyclic voltammetry (CV) measurements was performed on CVS instrument (797 VA Computrace, Metrohm). A platinum (Pt) rotating disk electrode (RDE) with a diameter of 3 mm and a Pt bar were used as the working electrode and the counter electrode, respectively. The reference electrode, (Ag/AgCl, 3 mol/L KCl), was placed in a small Teflon tube that contained 1 mol/L KNO3 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. All CV measurements were carried out by forward scan from 1.625 to −0.250 V vs. Ag/AgCl, followed by a reverse scan from −0.250 to 1.625 V vs. Ag/AgCl, at a scan rate of 0.1 V/s.

In order to study the adsorption mechanism of EPE2900 on the cathode surface during the copper electrodeposition, the other series of CV measurements were carried out by using Pt/Pt rotating ring-disk electrode (RRDE) as the working electrode. This designed experiment can provide direct evidence of the formation of Cu+−EPE2900 or Cu2+−EPE2900−Cl−. The Pt/Pt RRDE dimensions are: Pt disk radius r1 = 4.57 mm, Pt ring inner radius r2 = 4.93 mm and outer radius r3 = 5.38 mm. A Pt plate with an area of 1 cm² was used as the counter electrode and reference electrode, respectively. The potential on the disk was swept from 1.0 to −0.6 V vs. SMSE and then back to 1.0 V vs. SMSE, at a scan rate of 5 mV/s. Each CV measurement was recorded successive three cycles, marked as cycle 1, cycle 2 and cycle 3, respectively. In the meantime, the ring potential was kept at 0.2 V vs. SMSE which was positively high enough to oxidize Cu+ to Cu2+ on the ring electrode. The rotation speed of the RRDE was maintained at 1000 rpm during CV measurements.

Virgin make-up solution (VMS) for all the CV measurements was composed of 220 g/L CuSO4·5H2O and 55 g/L H2SO4. EPE2900, a triblock copolymer with the structure of polyethylene oxide (PEO)-polypropylene oxide (PPO)-polyethylene oxide (PEO), was provided by BASF Corp. It has a nominal molecular weight of 2900, containing ca. 40 wt% EO. It could be briefly represented by the formula of EO13PO30EO13. Cl− was added as NaCl with a purity of 99.95%. The temperature of the plating solution during CV measurement was maintained at 25 °C.

3. Results and discussion

3.1. Interpretations of CV plots and the definition of Q/Q0

The typical CV plots measured in VMS containing 200 ppm EPE2900 without or with 5 ppm Cl− are shown in Fig. 1a and Fig. 1b, respectively. It can be observed from Fig. 1a that the current density increases sharply at potentials below −0.2 V vs. Ag/AgCl in the absence of Cl−, indicating the desorption of adsorbed EPE2900 molecules from the cathode [25]. Therefore, the potential of −0.2 V vs. Ag/AgCl is the critical potential of EPE2900 desorption in VMS containing 200 ppm EPE2900. In the contrast, the reverse scan exhibits an obvious hysteresis, revealing a slow re-adsorption process of EPE2900 [25].

After adding the Cl− into EPE2900 solution, the CV curve obtained in VMS containing 200 ppm EPE2900 and 5 ppm Cl− demonstrates a more negative critical potential of EPE2900 desorption and a weaker hysteresis effect, as shown in Fig. 1b. The more negative critical potential can be explained by two possible reasons. Firstly, the adsorption strength of EPE2900 is enhanced by the addition of Cl−. Secondly, the amount of EPE2900 adsorption on the cathode is increased in the presence of Cl−. Taking the weaker hysteresis caused by the addition of Cl− into consideration, the increase of the adsorption strength of EPE2900 may be a dominant factor, leading to the differences between the two plots. On the other hand, plenty of EPE2900 molecules can adsorb onto the cathode due to electrostatic interaction and Van der Waals forces during copper electroplating, and thus the introduction of Cl− into the VMS should not lead to a significant rise in the amount of EPE2900 adsorption. Therefore, the adsorption mechanism of EPE2900 on the cathode can be tuned by varying the addition of Cl−, which maximizes the adsorption strength of EPE2900. Consequently, the critical potential of EPE2900 desorption shifts negatively and the hysteresis of CV plots becomes insignificant.

In the meantime, the copper deposited on the cathode begins to dissolve when the potential positively sweeps to 0.05 V vs. Ag/AgCl as also shown in Fig. 1. Obviously, two peaks attributed to copper stripping are observed at the potential range from 0.05 to 0.4 V vs. Ag/AgCl. The integral values measured with the Cu stripping peaks shown in Fig. 1a and Fig. 1b are defined as Q0 (EPE2900) and Q (EPE2900 and Cl−), respectively. The measured value of Q is

![Figure 1](https://example.com/home.png)

Fig. 1. Typical CV plots measured in the VMS: (a) containing 200ppm EPE2900; (b) containing 200 ppm EPE2900 and 5 ppm Cl−. The integrated values of the corresponding Cu stripping peaks are recorded as Q0 and Q, respectively. The integral interval is [0.05, 0.4].
smaller than $Q_0$, which is in good agreement with the discussion above. Because each Cl$^{-}$ concentration corresponds to different $Q$ value, the value of $Q/Q_0$ can be used to evaluate the suppression strength of EPE2900 measured in the VMS containing different Cl$^{-}$ concentrations. In principle, the smaller $Q/Q_0$ value corresponds to the stronger suppression strength, and this indicator is also effective when evaluating the suppression strength of EPE2900 at various concentrations.

3.2. Dependence of $Q/Q_0$ values on Cl$^{-}$ concentrations

With a constant concentration of EPE2900 in the VMS, $Q/Q_0$ values were determined as a function of Cl$^{-}$ concentrations. The measured results can be divided into four groups, as shown in Fig. 2. In the VMS containing 5 ppm EPE2900 (Fig. 2a), the successive addition of Cl$^{-}$ leads to the continuous increase of $Q/Q_0$ values. It indicates that the presence of Cl$^{-}$ can increase the rate of copper deposition. This is in good agreement with the literature reporting that Cl$^{-}$ is a good depolarizer for copper deposition [22,26]. In contrast to the results displayed in Fig. 2a, the $Q/Q_0$ values calculated from the solution containing 20 ppm EPE2900 presented in Fig. 2b decrease quickly with adding Cl$^{-}$. However, this phenomenon attests a possible synergistic effect between EPE2900 and Cl$^{-}$ on inhibiting copper deposition only occur when the concentration of EPE2900 is sufficient and cannot be easily observed at a very low EPE2900 concentration (5 ppm). Thus, the depolarization effect caused by Cl$^{-}$ is overwhelmed by the synergistic inhibiting effect between EPE2900 and Cl$^{-}$ at high EPE2900 concentration. The synergistic effect between EPE2900 and Cl$^{-}$ was discussed in details in our previous reports [22].

It can be found that $Q/Q_0$ values shown in Fig. 2c and Fig. 2d have a similar trend as exhibited in Fig. 2b. When Cl$^{-}$ concentration increases from 0 to 6 ppm, a sharp and linear decrease of the $Q/Q_0$ values is observed. After that, the decreasing rate of $Q/Q_0$ values becomes slow, even though the incremental step of Cl$^{-}$ increases to 5 ppm. Interestingly, the higher concentration of EPE2900 in the VMS, the more obvious differences can be seen between the two parts in each plot, as shown in Fig. 2c and Fig. 2d. According to Fig. 2, each plot, except Fig. 2a, reveals an inflection point at about 5 ppm Cl$^{-}$. Thus, it is reasonable to believe that there exists a critical Cl$^{-}$ concentration corresponded to a critical adsorption status of EPE2900 on the cathode. From the fundamental point of view, a reliable method is highly desired to determine the critical Cl$^{-}$ concentration for EPE2900 adsorption. In this work, linear fitting for crossing point (LFFCP) method is employed to determine the critical Cl$^{-}$ concentration. In particular, linear fitting is carried out for the both initial five points and the last five points in each plot. In doing so, the crossing point of the two fitting straight lines can be calculated. Thus, the obtained abscissas are the critical Cl$^{-}$ concentrations and are marked in each plot for the corresponding EPE2900 concentrations. Interestingly, these values are almost the same around 4.85 ppm. The independence of EPE2900 concentration indicates that the adsorption of EPE2900 on the cathode can reach a critical adsorption status with the assistance of 4.85 ppm Cl$^{-}$ in solution.

3.3. Dependence of $Q/Q_0$ values on EPE2900 concentrations

As shown in Fig. 3, the dependence of $Q/Q_0$ values on EPE2900 concentrations is determined in VMS containing 4.85 ppm Cl$^{-}$. Suppression strength of EPE2900 is found to be monotonously increased with the successive addition of EPE2900. Especially, the decline of $Q/Q_0$ values caused by the increase of EPE2900 concentration obviously can be divided into two distinct stages, similar to that observed in Fig. 2. Likewise, LFFCP method is also used to determine the adsorption amount of EPE2900 at the critical adsorption status. In this case, linear fitting is performed on these scattered points except for the initial three ones. That is because the synergistic effect between Cl$^{-}$ and EPE2900 cannot be well correlated to the values of $Q/Q_0$, when the concentration of EPE2900 is relatively low.
As marked in Fig. 3, the coordination of the crossing point is (11.02, 0.30), which means that the minimum concentration of EPE2900 needed to reach the critical adsorption status is ca. 11.02 ppm in the presence of 4.85 ppm Cl\(^-\). In order to verify this value, a series of plots are measured in the VMS containing different Cl\(^-\) concentrations, as exhibited in Fig. 4. It can be observed that the corresponding abscissas of these crossing points are almost the same (ca. 11.50), demonstrating that the required EPE2900 concentration for the critical adsorption status is independent of the Cl\(^-\) concentration. Specifically, the average value of all the calculated EPE2900 concentrations is 11.46 ppm. Hence, the critical adsorption status of EPE2900 and Cl\(^-\) can be achieved in the VMS containing critical concentrations for EPE2900 (11.46 ppm) and Cl\(^-\) (4.85 ppm), respectively.

3.4. A possible adsorption model of EPE2900 on the cathode

It is well known that Cl\(^-\) is an indispensable component in acid copper plating. It is able to interact with the suppressor and Cu\(^+\) to form a complex of Cu\(^+\)-suppressor-Cl\(^-\), which can strongly adsorb onto the cathode to inhibit reduction of Cu\(^2+\) during the copper deposition [25,27,28]. In addition, EPE2900 molecules can form micelles in aqueous solution, which are composed of the hydrophilic shell (PEO segments) and the hydrophobic core (PPO segments) [29,30]. Based on our testing data, a possible adsorption model of EPE2900 on the cathode is proposed, as illustrated in Fig. 5.

When Cl\(^-\) is absent in VMS, EPE2900 can only adsorb onto the cathode by electrostatic and Van der Waals forces, as displayed in Fig. 5a1. However, this adsorption strength is too weak to effectively inhibit copper deposition during microvias filling. That is the reason that Cl\(^-\) must be introduced into the VMS to improve the adsorption strength of EPE2900. With the increase of Cl\(^-\) concentration, more and more EPE2900 molecules begin to adsorb onto the cathode due to an anchoring effect of Cl\(^-\), greatly enhancing the adsorption strength or suppression strength of EPE2900. When the Cl\(^-\) concentration is increased to the critical value at 4.85 ppm (EPE2900 concentration is 11.46 ppm), the adsorption model of EPE2900 discussed above appears, as illustrated in Fig. 5a2. It can be observed that an intact barrier layer is formed on the cathode. Moreover, there are only two Cl\(^-\) ions to anchor one EPE2900 molecule, which can be attributed to the low concentration of Cl\(^-\) [25]. When Cl\(^-\) concentration is higher than 4.85 ppm, there will be more Cl\(^-\) ions attaching to an EPE2900 molecule, as shown in Fig. 5a3. This change will further enhance the adsorption strength of EPE2900, thus providing stronger inhibiting effect on copper deposition. The transition of EPE2900 adsorption models from Fig. 5a1 to Fig. 5a3, resulted from an increase of Cl\(^-\) concentration, is in good agreement with the trend of the plots presented in Fig. 2.

When EPE2900 concentration in VMS is lower than 11.46 ppm, as shown in Fig. 5b1, the barrier layer formed on the cathode is not continuous, which Cl\(^-\) and Cu\(^2+\) are still able to diffuse to the cathode surface easily. Therefore, the following addition of Cl\(^-\) into the VMS may significantly enhance the copper deposition, due to the depolarization role of Cl\(^-\). This hypothesis can be used to explain the increased Q/Q\(_0\) values shown in Fig. 2a. When EPE2900 concentration approaches 11.46 ppm, the critical adsorption status appears as exhibited in Fig. 5b2 (same as Fig. 5a2). In this model, it is assumed that EPE2900 molecules can only form a monolayer

---

**Fig. 3.** Q/Q\(_0\) as a function of EPE2900 concentration measured in the VMS containing 4.85 ppm Cl\(^-\).

**Fig. 4.** Q/Q\(_0\) as a function of EPE2900 concentration measured in the VMS containing different Cl\(^-\) concentrations: (a) 30 ppm; (b) 60 ppm; (c) 90 ppm; (d) 120 ppm.
adsorption at the critical concentration of 11.46 ppm. Therefore, increasing EPE2900 concentration from 0 to 11.46 ppm leads to more and more EPE2900 molecules adsorbing onto the cathode due to the anchoring effect of Cl⁻. This will greatly enhances the suppression strength of EPE2900 on inhibiting copper deposition. In the meantime, a multilayer adsorption of EPE2900 on the cathode is very likely, as described in Fig. 5b3. Consequently, the diffusion of Cu²⁺ from the bulk solution to the cathode surface becomes more difficult, resulting in further increased suppression strength. However, it is worth noting that the enhancement of suppression strength caused by the increase of EPE2900 concentration during multilayer adsorption is much smaller than that in monolayer adsorption. In the case of monolayer adsorption, EPE2900 molecules inhibit copper deposition mainly by occupying the active sites. Multilayer adsorption of EPE2900 inhibits copper deposition predominantly by preventing the accessibility of Cu²⁺ to cathode surface. Hence, the proposed adsorption model can clearly elucidate the measured results shown in Fig. 3 and Fig. 4.

3.5. Verification of the proposed adsorption model

As discussed above, an adsorption model for the transition of EPE2900 on the cathode surface is proposed based on CVS results as well as the relevant characteristics of polyethylene glycol (PEG). A further verification of the formation of Cu⁺-EPE2900 or Cu⁺-EPE2900-Cl⁻ complex during the adsorption process is required. The Cu⁺ is an intermediate during the copper electrodeposition process in an acid solution, which is unstable in the plating bath and in the atmosphere [31]. A direct detection of the complex containing Cu⁺, thus, is very hard. In this work, RRDE techniques, well known by its advantage in detection of intermediates, are employed to provide evidence of the existence of the Cu⁺-containing complex.

As shown in Fig. 6a and Fig. 6b, the CV plot measured in VMS during the first cycle (Cycle 1) is almost overlapped with the subsequent two cycles (Cycle 2 and Cycle 3). However, this circumstance is obviously changed when EPE2900 or EPE2900 + Cl⁻ is added into VMS. In particular, the potential of copper deposition observed in
cycle 1 is shifted to negative direction in cycle 2 and 3. The potential difference indicates that the copper deposition is hindered and needs larger overpotential after adding EPE2900 or EPE2900 + Cl−. More importantly, the enhanced suppression effect during the cycle 2 and 3 is related to some species, most likely Cu+, produced during the first cycle.

During the copper deposition process in VMS, an obvious current-potential (I-E) hysteresis can be observed in the successive three cycles, which is caused by the different substrates in the forward (Pt substrate) and reverse (Cu substrate) scans. However, the I-E hysteresis obtained in VMS containing EPE2900 is dominated by the adsorption and desorption process of EPE2900, which has been discussed above. In addition, it can be observed that copper deposition is more difficult during the cycle 2 and 3, compared to during the cycle 1, which may be caused by the different species adsorbed on the disk. In the cycle 1, the adsorbed species on the disk at the beginning of copper deposition is EPE2900 without any doubt, whereas it may become Cu+-EPE2900 in the cycle 2 and 3.

As shown in Fig. 6c, Cu+, as an intermediate, is detected during the both copper electrodeposition and copper dissolution processes. It should be noted that the Cu+ peaks measured in VMS + EPE2900 during the copper dissolution are much larger than that obtained in VMS. In the meantime, during copper dissolution process, the corresponding copper stripping peaks measured in VMS + EPE2900 are smaller than that in VMS (shown in Fig. 6a). Thus, the addition of EPE2900 can enhance the stability of Cu+ in VMS.

As listed in Table 1, the charge calculated on the disk electrode during cathodic and anodic processes are recorded as Qr,a (Qring,anodic) and Qr,c (Qring,cathodic) respectively. Similarly, the charge calculated at the ring electrode during cathodic and anodic process are recorded as Qr,c (Qring,cathodic) and Qr,a (Qring,anodic), respectively. It can be observed from Table 1 that the values of Qr,c/Qr,a and Qr,a/Qd,a calculated in VMS containing EPE2900 are much larger than those obtained in VMS, attesting that EPE2900 can react with Cu+ to form a stable complex of Cu+-EPE2900 [32]. It is worth noting that the value of Qd,a is slightly larger than Qd,a in VMS, which can be explained by three reasons. Firstly, Cu+ is captured by the ring electrode. Secondly, Cu+ has undergone a disproportionation reaction. Thirdly, Cu+ exists in the electrolyte after one cycle is completed. In VMS containing EPE2900, Cu+ is likely present as Cu+-EPE2900 after one cycle is completed, which can be adsorbed onto the Pt disk to inhibit copper deposition in the subsequent cycles. In addition, it can be observed from Fig. 6d that the detected Cu+ peak at ring electrode during the cycle 1 is larger than those of subsequent two cycles. This is due to the relatively stronger adsorption strength of Cu+-EPE2900, relative to EPE2900. As shown in Fig. 6a, the copper deposition potential measured in VMS containing EPE2900 + Cl− is more negative than those either in VMS or in VMS containing EPE2900. This result suggests that there is a synergistic effect between EPE2900 and Cl− to enhance inhibition for the copper deposition [33–35]. Cl− can act as an anchor for strengthening the adsorption of EPE2900. On the other hand, Cu+, an intermediate during copper deposition
and dissolution, is likely to be involved in the adsorption model of EPE2900. Cu⁺ is usually produced at a relatively positive potential about -0.4 V vs. SMSE [36,37]. As shown in Fig. 6b, a manifested valley appears when the potential scans from -0.30 to -0.55 V vs. SMSE in cycle 1. A reasonable explanation for this phenomenon is that the generated Cu⁺ can interact with EPE2900-Cl⁻ forming a new complex (Cu⁺-EPE2900-Cl⁻). As shown in Table 1, the Qr,c/Qd,c and Qr,a/Qd,a calculated from VMS and EPE2900 and Cl⁻ are much larger than those from VMS, indicating that Cu⁺ ions react with EPE2900-Cl⁻ and form a stable complex. This complex has a stronger adsorption strength than Cu⁺-EPE2900 and shows no obvious desorption behavior even though the potential is lower than -0.6 V vs. SMSE. Thus, during the subsequent two cycles, the adsorbed species onto the disk is Cu⁺-EPE2900-Cl⁻ other than EPE2900-Cl⁻ or Cu⁺-EPE2900, which results in the negative shift of the potential for copper deposition.

4. Conclusions

A new triblock copolymer (EPE2900) was found to be effective to suppress the Cu electrodeposition for an application of microvia filling in electronic industries. In this work, the adsorption behavior of EPE2900 on the cathode during the copper electrodeposition process was systematically investigated using CVS methods. It was found that, within certain limits, the increase of both Cl⁻ and EPE2900 concentrations could enhance suppression strength of EPE2900 on inhibiting copper deposition. A LFFCP method was employed to calculate the critical concentrations of Cl⁻ and EPE2900, and the results indicated that 4.85 ppm Cl⁻ and 11.46 ppm EPE2900 were sufficient to reach the critical adsorption on the cathode. Importantly, a possible adsorption model of EPE2900 on the cathode was proposed to elucidate the measured electrochemical results. In the critical adsorption status, monolayer EPE2900 adsorbed onto the cathode and each EPE2900 molecule was anchored by two Cl⁻ ions. The proposed adsorption model was further verified by CV measurements using RRDE in different electrolytes. It was demonstrated that Cu⁺ could react with EPE2900 and form Cu⁺-EPE2900 complexes. Upon addition of Cl⁻, more stable complex of Cu⁺-EPE2900-Cl⁻ eventually formed.

Acknowledgements

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

References


Table 1

<table>
<thead>
<tr>
<th>Method</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
</tr>
</thead>
</table>

and dissolution, is likely to be involved in the adsorption model of EPE2900. Cu⁺ is usually produced at a relatively positive potential about -0.4 V vs. SMSE [36,37]. As shown in Fig. 6b, a manifested valley appears when the potential scans from -0.30 to -0.55 V vs. SMSE in cycle 1. A reasonable explanation for this phenomenon is that the generated Cu⁺ can interact with EPE2900-Cl⁻ forming a new complex (Cu⁺-EPE2900-Cl⁻). As shown in Table 1, the Qr,c/Qd,c and Qr,a/Qd,a calculated from VMS and EPE2900 and Cl⁻ are much larger than those from VMS, indicating that Cu⁺ ions react with EPE2900-Cl⁻ and form a stable complex. This complex has a stronger adsorption strength than Cu⁺-EPE2900 and shows no obvious desorption behavior even though the potential is lower than -0.6 V vs. SMSE. Thus, during the subsequent two cycles, the adsorbed species onto the disk is Cu⁺-EPE2900-Cl⁻ other than EPE2900-Cl⁻ or Cu⁺-EPE2900, which results in the negative shift of the potential for copper deposition.

4. Conclusions

A new triblock copolymer (EPE2900) was found to be effective to suppress the Cu electrodeposition for an application of microvia filling in electronic industries. In this work, the adsorption behavior of EPE2900 on the cathode during the copper electrodeposition process was systematically investigated using CVS methods. It was found that, within certain limits, the increase of both Cl⁻ and EPE2900 concentrations could enhance suppression strength of EPE2900 on inhibiting copper deposition. A LFFCP method was employed to calculate the critical concentrations of Cl⁻ and EPE2900, and the results indicated that 4.85 ppm Cl⁻ and 11.46 ppm EPE2900 were sufficient to reach the critical adsorption on the cathode. Importantly, a possible adsorption model of EPE2900 on the cathode was proposed to elucidate the measured electrochemical results. In the critical adsorption status, monolayer EPE2900 adsorbed onto the cathode and each EPE2900 molecule was anchored by two Cl⁻ ions. The proposed adsorption model was further verified by CV measurements using RRDE in different electrolytes. It was demonstrated that Cu⁺ could react with EPE2900 and form Cu⁺-EPE2900 complexes. Upon addition of Cl⁻, more stable complex of Cu⁺-EPE2900-Cl⁻ eventually formed.

Acknowledgements

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

References


