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Structural Effect of Polymers on Their Microvia Filling Performance as Suppressors During the Copper Electroplating

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Suppressors are crucial to microvia filling via Cu electrodeposition in electronic industry. In this work, two types of polymer suppressors with different structures (PEG6000 vs EPE2900) are compared in terms of their microvia filling performance during the Cu electrodepostion by using cyclic voltammetry (CV) measurements on rotating ring-disk electrode (RRDE). CV curves obtained on the disk electrode prove our previous conclusion that, compared to PEG6000, EPE2900 can more effectively inhibit Cu electrodeposition on the cathode. Importantly, the plots measured on the ring electrode provide solid evidence for the interaction between the suppressors and Cu^+. The addition of Cl^- can greatly enhance the adsorption strength of suppressor-Cu^+ complex due to the formation of suppressor-Cu^+-Cl^- complex. on the cathode surface, effectively inhibiting the copper deposition. According to the mechanism of the suppressors obtained from RRDE technique, the reasons for the stronger suppression strength of EPE2900 are elucidated by molecular dynamic (MD) simulations and Gaussian 03 program based on molecular structures, the electronegativity of oxygen atoms, and the steric hindrance for these two different suppressors. In good agreement with the theoretical studies, it has been experimentally demonstrated that the plating solution using EPE2900 as the suppressor shows better microvia filling performance than PEG6000 evidenced by the corresponding optical microscope images. More hydrophilic properties of the obtained copper layer by using EPE2900 is also advantageous over the PEG6000 as the suppressor.

Keywords: Microvia filling; Copper electroplating; Polymer suppressor; Rotating ring-disk electrode.

1. INTRODUCTION

Microvia filling is an important process during the production of printed circuit boards (PCBs), especially for fabricating high-density interconnection boards. It can be well achieved by Cu electrodeposition in the form of “bottom-up deposition” or “superfilling”[1-3]. However, the superfilling process cannot occur unless some functional additives are present in the plating solution[4-7]. One of the most important functional additives is the suppressor, which is usually composed of macromolecular polyether. According to convection-dependent adsorption mechanism[1], strong convection can greatly increase the flux of chloride ions to the cathode surface, being anchors for enhancing the adsorption of the suppressor, so as to inhibit the deposition rate of Cu. Because the convection on the board surface is relatively stronger than that in the microvias, such adsorption of the suppressors leads to well-defined superfilling in the microvia.

Up to now, the most common suppressor used for microvia filling by Cu electrodeposition is polyethylene glycol (PEG)[8-14]. It has been found that the filling performance of plating solution is a function of the molecular weight of PEG, when the mass concentration of PEG is fixed[15]. Moreover, it has been demonstrated that PEG, with a molecular weight of 6000-8000 g/mol, once showed the best performance in microvia filling[15]. Generally, the bigger molecular weight of PEG leads to stronger inhibiting effect on the Cu electrodeposition. Even that, the suppression strength of PEG remains insufficient unless chloride ions are present in the plating solution simultaneously. Surface-enhanced Raman spectroscopy indicated that the adsorption of PEG on the copper surface is associated with Cu^+ and Cl^-[16]. The real suppressor adsorbed onto the cathode is the complex of PEG-Cu^+-Cl^-, rather than PEG. Thus, PEG, as a suppressor used in microvia filling, has been extensively studied and applied during the last decade. However, two major weaknesses of the PEG still limit its application in the microvia filling. Apart from the weak suppression strength, hydrophobic Cu layer resulting from the PEG is inconvenient for subsequent processes (for example, tin-plating or etching).

Our recent efforts in exploring the efficient suppressors indicated that the triblock copolymer of EPE2900 is an effective suppressor for microvia filling[17,18]. In this work, the microvia filling performance was compared when PEG 6000 and EPE 2900 were used as the suppressors. Galvanostatic measurement is employed to compare the suppression strength of PEG6000 and EPE2900, whereas RRDE technique is introduced to gain more insight into their adsorption mechanisms on the cathode surface. The differences between PEG6000 and EPE2900 molecules are analyzed by theoretical calculations, providing convincing evidences for the stronger suppression strength of EPE2900. In addition, the hydrophilic-hydrophobic properties of the obtained copper layer after microvia filling are evaluated by contact angle experiments.

2. EXPERIMENTAL

Printed circuit boards with microvias (diameter of 150 μm and depth of 75 μm) were used as testing samples. The typical copper plating bath was composed of 220 g/L $CuSO_4 \cdot 5H_2O$, 55 g/L H_2SO_4, 60 ppm Cl^- (added as NaCl), 3 ppm bis(3-sulfopropyl) disulfide, 4 ppm Janus Green B and 200 ppm suppressor. The microvia filling performance was evaluated by cross-sectional views of the microvias using optical microscopy (DFC290, Leica). And the other details on copper plating process as well as the preparation of cross-sectional samples can be found in our previous work (reference 18).

Galvanostatic measurements were carried out on an electrochemical workstation (CHI 760D) in a three-electrode cell. A platinum rotating disk electrode (Pt-RDE, Pine) with a diameter of 5 mm was used as the working electrode. The counter electrode was a small copper bar, which was placed in a small glass tube containing only basic electrolyte without any additives. The end side of the small glass tube was sealed with a porous polymer material to avoid possible contamination. 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 basic electrolyte to prepare a Cu-RDE. The GMs were carried out at a current density of 2 A/dm^2 with the rotation speed of 1000rpm.

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

The basic electrolyte used for all the electrochemical measurements was composed of 220 g/L $CuSO_4 \cdot 5H_2O$ and 55 g/L H_2SO_4. The temperature was maintained at 25 °C during each measurement. EPE2900, a triblock copolymer with the structure of polyethylene oxide(EO) - polypropylene oxide(PO) - polyethylene oxide(EO), was provided by BASF Corp. (molecular weight 2900, ca. 40 wt% EO). It could be briefly represented by the formula of $EO_{13}PO_{30}EO_{13}$. Cl^- was added as NaCl with a purity of 99.95%.

Molecular dynamic simulations of PEG6000 and EPE2900 molecules in water solution were carried out by using Materials Studio (MS, form Accelrys Inc) software. The molecular dynamic simulations were performed at 298 K, NVT ensemble and COMPASS force field, with a time step of 1 fs and simulation time of 1 ns. The electronegativity of the oxygen atoms contained in the suppressors were calculated by Gaussian 03 program, employing the hybrid Becke exchange and Lee, Yang, and Parr correlation (B3LYP) functional method. In this work, 6-311G(d,p) basis sets were used for hydrogen, oxygen and carbon atoms.

The wettability of the deposited copper surface was evaluated by the sizes of contact angle, which was performed by OCA20 (Data Physics Instruments) using a droplet (3 μL) of water as an indicator.

3. RESULTS AND DISCUSSION

Fig. 1 shows the cross-sectional views of the microvias after electroplating in the plating bath using PEG6000 and EPE2900 as the suppressors, respectively. It can be observed that the microvia obtained in the solution using PEG6000 as the suppressor is filled by deposited copper with a large dimple. In contrast, the microvia is fully filled by deposited copper without a dimple after electroplating in the solution using EPE2900, which has been demonstrated in our previous work[18]. In addition, contact angle measurements are employed to evaluate the wettability of different samples, as shown in Fig. 2. When the aging time of the sample is prolonged, the size of contact angle is gradually increased. That means the wettability of the copper surface becomes poor. However, it should be noted that the sample obtained in the plating solution using EPE2900 as the suppressor always shows smaller contact angle than that using PEG6000 as the suppressor. And the resulting hydrophilic surface will facilitate the following process during PCB processing.All the above results indicate that EPE2900 is a better suppressor for microvia filling by Cu electrodeposition.

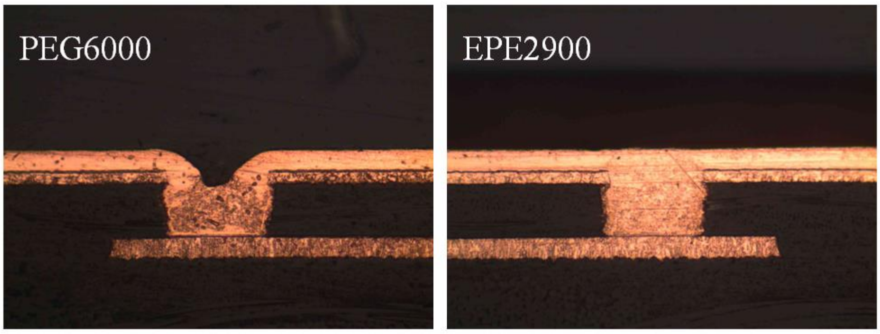

Figure 1. Optical microscope images of microvias after electroplated in typical plating bath containing different suppressors. All the images are magnified 200×.

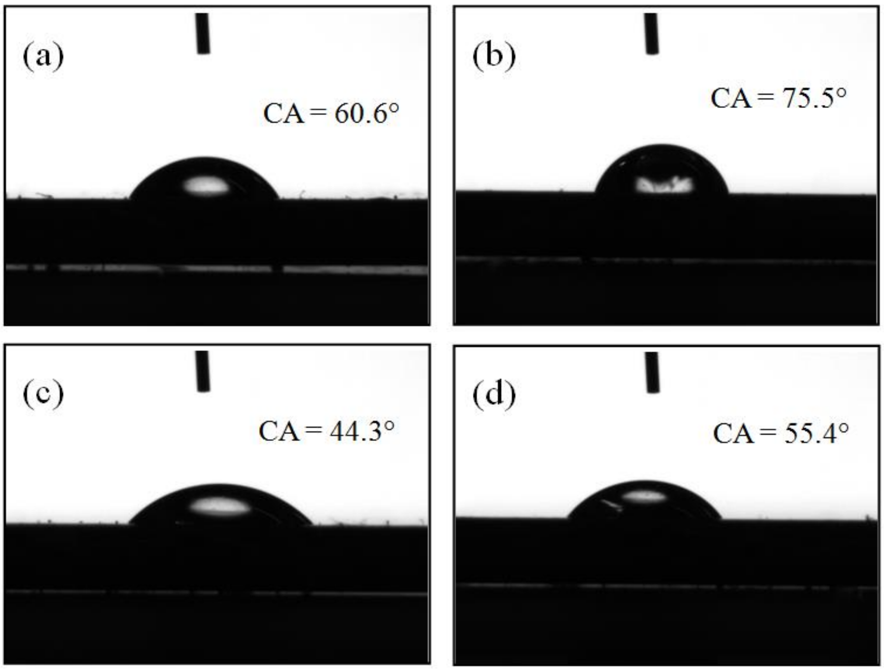

Figure 2. Water contact angle measurements on the copper surface of different samples: (a) and (b) are the same sample obtained by using PEG6000 as the suppressor; (c) and (d) are the same sample obtained by using EPE2900 as the suppressor. (a) and (c) are the as-prepared samples, whereas (b) and (d) are the samples exposed in the air for 120 h.

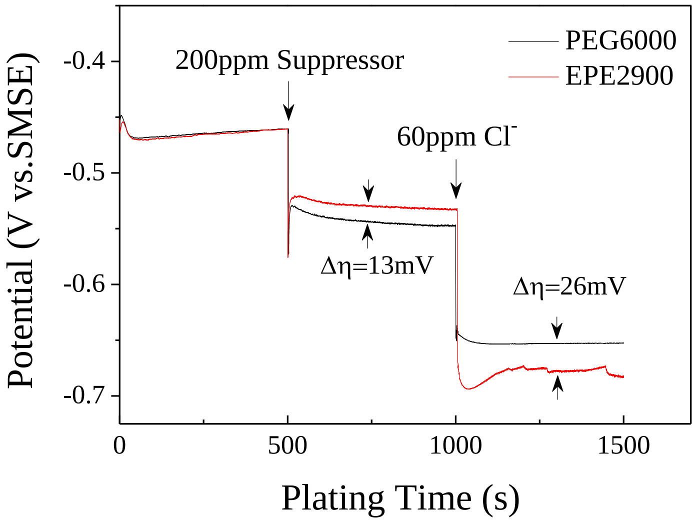

Figure 3. Galvanostatic measurements in basic electrolyte with successive additions of the suppressor and Cl$^-$.

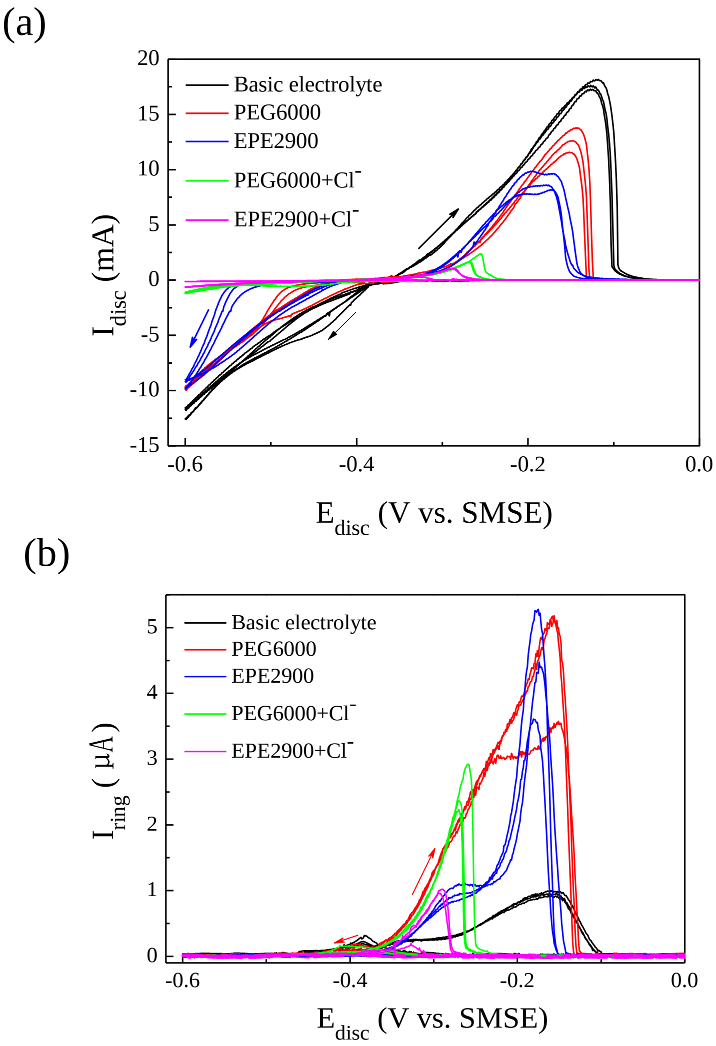

Figure 4. (a) Cyclic voltammetry plots measured on the disk electrode in different electrolytes; (b) I-E plots measured on the ring electrode in different electrolytes; The amounts of the suppressor and Cl$^-$ used in the measurement are 200 ppm and 60 ppm, respectively.

To find the reasons resulting in the differences between EPE2900 and PEG6000, galvanostatic measurements are carried out in a three-electrode cell, and the corresponding results are shown in Fig. 3. It can be observed that an obvious potential drop appears after the suppressor is added into the basic electrolyte.

Compared to PEG6000, the potential drop caused by the addition of EPE2900 is less significant (the potential difference $\Delta\eta$ = 13mV), suggesting that the suppression strength of EPE2900 on inhibiting Cu electrodeposition is weaker than that of PEG6000 in basic electrolyte only containing suppressors. As the successive addition of Cl^-, the potential of Cu electrodeposition continues to shift negatively. It should be noted that the potential drop caused by the addition of Cl^- is much larger than that by the suppressor. This phenomenon is in good agreement with the reported results that Cl^- can greatly enhance the suppression strength of the suppressor. That indicates there exists a synergistic inhibiting effect between the suppressor and Cl^-[17,19]. Furthermore, the potential drop caused by adding Cl^- into the solution with EPE2900 as the suppressor is found to be larger than that in the solution using PEG6000 as the suppressor, which indicates that the synergistic effect between EPE2900 and Cl^- is stronger than that between PEG6000 and Cl^-. In addition, the final potential of Cu deposition measured in the solution containing EPE2900 and Cl^- is more negative than that in the solution containing PEG6000 and Cl^-, suggesting that the suppression strength of EPE2900 is stronger than that of PEG6000 in the presence of Cl^-[18].

As discussed above, during Cu electrodeposition process in the solution using PEG6000, the real suppressor is the complex of PEG-Cu^+-Cl^-[20]. Obviously, Cu^+, the intermediate product during Cu electrodeposition, is indispensable to the barrier layer (composed of PEG-Cu^+-Cl^-). In this work, RRDE technique which is well known by its advantage in detection of the intermediates[21], are employed to study the adsorption mechanisms as well as the electrochemical properties of PEG6000 and EPE2900.

As shown in Fig. 4(a), when the suppressor is added into the basic electrolyte, the cathodic polarization of Cu electrodeposition becomes noticeable. Compared to PEG6000, EPE2900 shows stronger suppression strength on inhibiting Cu deposition in the absence of Cl^-. This result seems to conflict with that obtained in Fig. 3, which can be attributed to the different adsorption behaviors of the suppressors on different substrates of the working electrode (Cu electrode in Fig. 3 and Pt electrode in Fig. 4). However, it can be observed that in the presence of Cl^-, EPE2900 still shows stronger suppression strength than PEG6000, which is in agreement with the results obtained in Fig. 3. Therefore, it can be concluded that when the suppressor and Cl^- are simultaneously present in the solution, the inhibiting effect of EPE2900 is stronger than that of PEG6000 regardless of the substrate of the working electrode.

Fig. 4(b) shows the I-E plots measured on the ring electrode. It suggests that Cu^+, as an intermediate, is not only observed during Cu electrodeposition but also detected during Cu dissolution process. Moreover, the Cu^+ peak measured during Cu deposition process is much smaller than that during Cu dissolution process, which can be attributed to the rate-determining step of $Cu^{2+} + e^- \rightarrow Cu^+$ and $Cu^+ - e^- \rightarrow Cu^{2+}$ in Cu deposition and dissolution processes, respectively[22,23]. From Fig. 4(a), it is obvious that the Cu stripping peak measured in the basic electrolyte containing only PEG6000 is smaller than that in the basic electrolyte. However, as shown in Fig. 4(b), the corresponding Cu^+ peak detected in the basic electrolyte containing PEG6000 is much larger than that in the basic electrolyte. These results not only demonstrate that PEG6000 indeed has an inhibiting effect on Cu electrodeposition process, but also indicate that PEG6000 can interact with Cu^+ to form a relatively stable complex[22], such as PEG6000-Cu^+, which can improve the stability of Cu^+ in the plating solution. Compared to the plots measured in basic electrolyte or basic electrolyte only containing PEG6000, the Cu stripping peak measured in basic electrolyte containing PEG6000+Cl^- exhibits a sharp decrease, demonstrating the synergistic effect between PEG6000 and Cl^- on inhibiting Cu electrodeposition. Take PEG6000 complexing with Cu^+ to form PEG6000-Cu^+ into consideration, a possible explanation for the synergistic effect is that PEG6000 can react with Cu^+ and Cl^- to form a complex of PEG6000-Cu^+-Cl^-. This complex can strongly adsorb onto the cathode and shows a stronger inhibiting effect than PEG6000 or PEG6000-Cu^+.

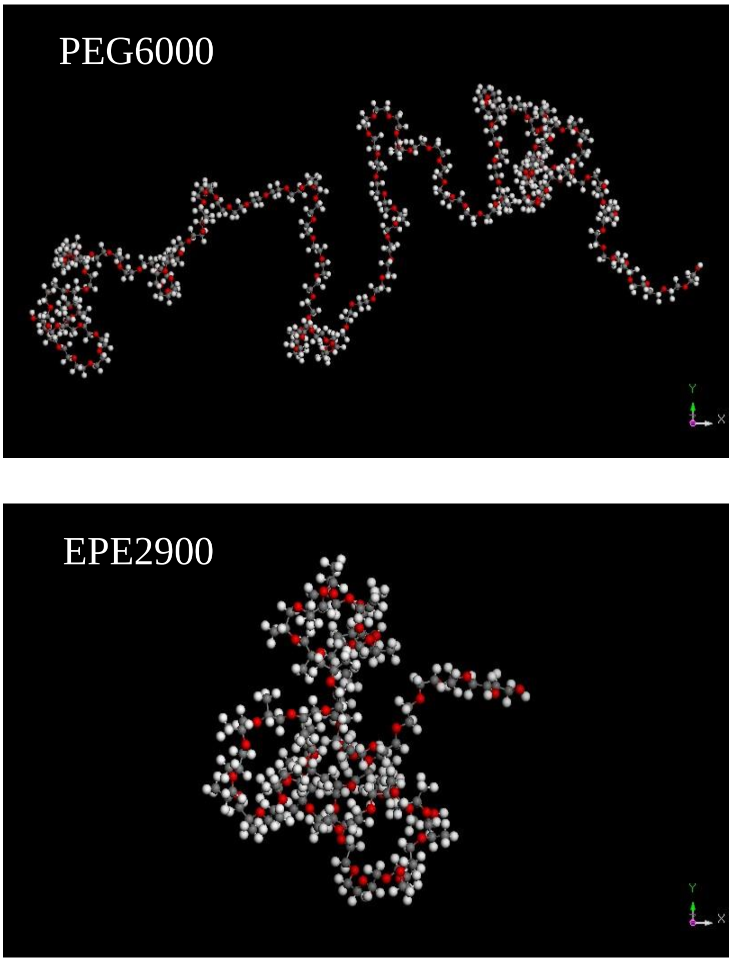

Figure 5. Steric configurations of the suppressor molecules in water solution after molecular dynamic simulations.

Compared to PEG6000, EPE2900 reveals the similar plots as shown in Fig. 4. It can be concluded that the electrochemical behaviors of EPE2900 on the cathode are similar to that of PEG6000, that is, EPE2900 can also react with Cu^+ and Cl^- to form EPE2900-Cu^+ or EPE2900-Cu^+-Cl^-

complex. However, the suppression strength observed with EPE2900 is much stronger than that on PEG6000.

In order to understand the root causes of the stronger suppression strength of EPE2900, molecular dynamic simulations in water solution are performed by Materials Studio software, as illustrated in Fig. 5.

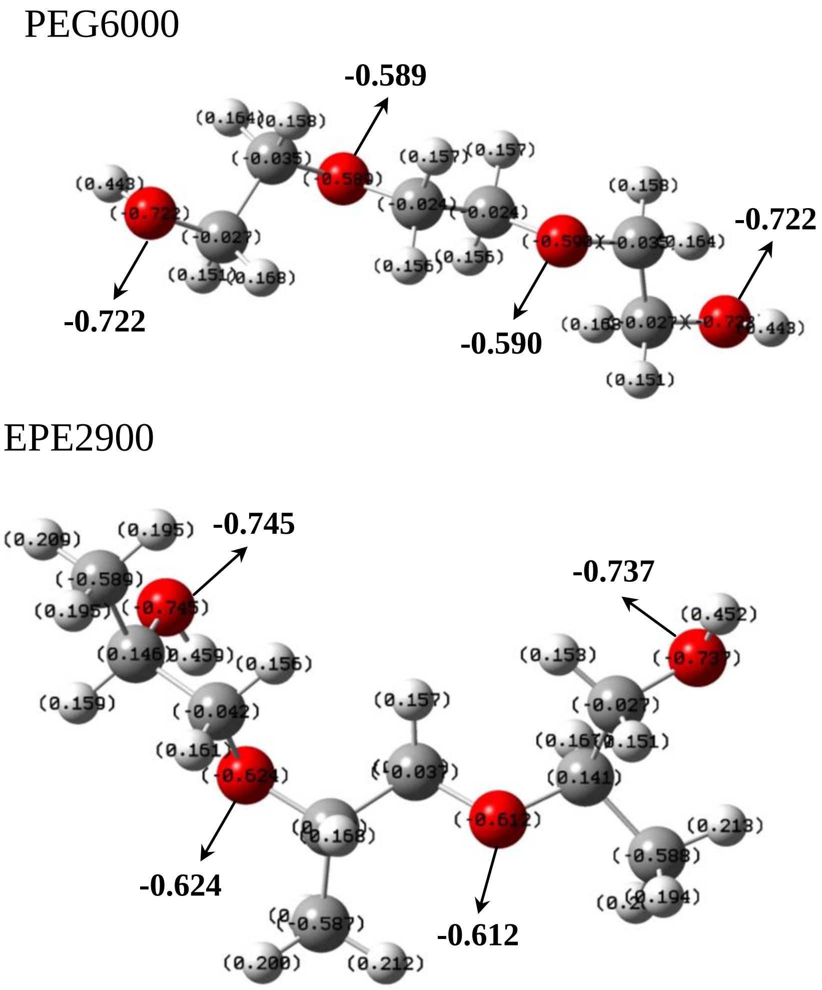

Figure 6. Optimized geometries and natural bond orbital charge distributions for the segments of the suppressor molecules.

It can be seen that PEG6000 molecule has a linear structure whereas EPE 2900 shows a clustered structure. In principle, the suppressor with the clustered structure is prone to form a compact and thick barrier layer adsorbed onto the cathode. Gaussian 03 program is then employed to calculate the electronegativity of the oxygen atoms in the suppressors, as shown in Fig. 6. Noteworthy, the electronegativity of the oxygen atoms in EPE2900 molecule is stronger than that in PEG6000 molecule. As a result, Cu^+ will preferrably coordinate with the oxygen atoms in EPE2900 molecules to form EPE2900-Cu^+ complex (EPE2900-Cu^+-Cl^- complex in the presence of Cl^-). Consequently, the adsorption strength of EPE2900 on the cathode should be stronger than that of PEG6000. On the other hand, the PEG6000 molecules can be considered to be constituted by ethylene oxide, whereas

EPE2900 molecules are composed of ethylene oxide and propylene oxide segments. Because propylene oxide contains a branched methyl, the introduction of propylene oxide segments may increase the steric hindrance of EPE 2900 molecules for preventing Cu^{2+} diffusing to the cathode surface. In our opinions, it is the differences in molecular structures, electronegativity of oxygen atoms, and the steric hindrance that result in the adsorbed EPE2900 molecules showing stronger suppression strength than PEG6000 on inhibiting copper deposition.

4. CONCLUSIONS

In this work, the differences between EPE2900 and PEG6000 in microvia filling by copper electroplating are evaluated by the microvia filling performance and wettability of the deposited copper surface. And the results indicate that the plating solution using EPE2900 as the suppressor shows better microvia filling performance than that with PEG6000. In addition, the obtained copper layer by using EPE2900 as the suppressor is more hydrophilic. All these results indicate that EPE2900 is a promising suppressor in microvia filling by copper electrodeposition.

Then, the reasons for the differences between the two suppressors are investigated in detailed. The results of galvanstatic measurements and cyclic voltammetry demonstrate that the EPE2900 leads to stronger suppression strength relative to that of PEG6000. The Cu^+ peak measured on the ring electrode indicates that both PEG6000 and EPE2900 can interact with Cu^+ to form complex. When Cl^- is present in the plating solution, the suppressor can react with Cu^+ and Cl^- to form suppressor-Cu^+-Cl^- complex. This complex adsorbs onto the cathode to form a barrier layer which can strongly inhibit Cu electrodeposition. Furthermore, the reasons for the stronger suppression strength of EPE2900 can be attributed to the differences in molecular structures, electronegativity of oxygen atoms, and the steric hindrance.

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