Copolymer of Pyrrole and 1,4-Butanediol Diglycidyl as an Efficient Additive Leveler for Through-Hole Copper Electroplating

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ABSTRACT: A copolymer comprising of pyrrole and 1,4-butanediol diglycidyl ether (PBDGE) was designed and synthesized as a leveler to improve the throwing power for printed circuit board (PCB) through-hole electroplating. The results of linear sweep voltammetry (LSV), galvanostatic measurements (GMs), and cyclic voltammetry (CV) reveal the strong coordination effect of PBDGE with other additives and confirm the advantageous performance of PBDGE to effectively assist the electroplating of through-hole. An increment of 35.5% in the throwing power was achieved under the addition of PBDGE in through-hole plating. Additionally, the reaction mechanism was studied by quantum chemical calculations and molecular dynamics (MD) simulations, indicating that the pyrrole rings of the PBDGE molecule are adsorbed on the copper surface as the adsorption sites to balance the copper plating regardless of the through-hole position differences.

INTRODUCTION

Recently, printed circuit boards (PCBs) with high-density interconnection (HDI) have received a lot of attention due to the wide application in 5G communication, wearable devices, and other booming fields.1−5 As is well known, the copper electrodeposition in acidic electrolytes plays a critical role in PCB manufacture.5−7 The copper electroplating of the through-holes (THs) is especially performed to obtain the conductive interconnection between the layers in multilayer PCB. The growing complexity of electronic products promotes the development of HDI technology and puts forward higher quality requirements for the copper coating of TH.6−11 Nevertheless, there are still several challenges to meet the electronic product trend of miniaturization, integration, and portability.

To establish a reliable system performance, it is crucial to achieving a highly reliable conductive coating with uniform thickness. As for THs, the uniform coating thickness of TH means that the thickness of the center (low current density) is close to the one at the mouth (high current density). However, there are two major issues affecting the uniformity of TH metallization, which are inhomogeneous current distribution and the different transfer rates of metal ions and additives.8 Accordingly, particular organic additives were developed to meet the requirement of the stepless coating thickness in different current density regions of the TH.9,10,12−17

Generally, organic additives are classified as an accelerator, such as bis-(sodium sulfiopropyl)-disulphide (SPS), inhibitor, including poly(ethylene glycol) (PEG), and leveler, such as Janus Green B (JGB).10,12 The effect of additives in the electroplating bath is not a simple superposition of the effects of each single component additive but a result of complex synergistic or anticompetitive effects among them. The synergistic effect among additives mostly originates from their adsorption and migration characteristics under chloride ions and the competition between the suppressor, accelerator, and leveler.13−16 It is generally believed that Cl− can act as a synergistic inhibitor to hinder the copper electrodeposition.8,13,14 There is a strong interaction between the accelerator and the metal surface. In the presence of Cl−, the accelerator has a strong adsorption effect on the copper surface.18,19 It has been confirmed that SPS−Cl− is an accelerator for copper electrodeposition.13−16 Zhu et al.20 found that SPS adsorption on copper surface is not related to the convection and ethylene oxide/propylene oxide (EO/PO) is proportional to convective intensity. With the increase of convective intensity, there is a competitive relationship between EO/PO and SPS adsorption. Dow et al.21 documented the synergistic effect of PEG−SPS−diazine black (DB)−Cl− and found DB and PEG−Cl− have no synergistic effect on the inhibition of copper electrodeposition, whereas JGB is capable of doing that. In the presence of PEG, DB can still significantly inhibit the promotion effect of SPS in copper electrodeposition with the existence of chloride ions.
In several recent studies, the importance of leveler has been highlighted.22−25 The leveler increases the polarization of the electrode to inhibit the electrodeposition of copper, resulting in a uniform copper coating. Usually, the levelers involved in copper electrodeposition are nitrogen-containing or quaternary ammonium compounds including dye molecules (e.g., JGB),26 quaternary ammonium surfactants,27 and copolymers.28 The dye molecules, however, are unstable in the electroplating bath because of the spontaneous decomposition.29 Recently, quaternary ammonium surfactants have attracted a lot of interest.7,22,27 It was found that pyrrole derivatives tend to adsorb to the cathode in electroplating because of the electrophilic aryl ring of pyrrole, which is supported by molecular dynamics (MD) simulation and quantum chemical calculations.30

Throwing power (TP) is an important index to evaluate the leveling ability of levelers.7 The results of through-hole plating are characterized by cross-sectional images of the THs obtained by a metalloscope (Olympus BX51). Generally, the value of TP is calculated by the six-point method expressed by eq 1

\[
TP = \frac{2 \times (h_a + h_f)}{h_a + h_b + h_c + h_d} \times 100\%
\]

where \( h_a, h_b, h_c, \) and \( h_d \) are the electroplating thicknesses at the surface of the TH; \( h_e \) and \( h_f \) are the electroplating thicknesses at the center of the TH, respectively, as shown in Figure 1.

![Figure 1](https://example.com/f1.png)

**Figure 1.** Diagram of the through-hole displaying the positions of measured points for TP calculation.

In this paper, the synthesis of a new leveler based on pyrrole and 1,4-butanediol diglycidyl ether (BDGE) was attempted. The effects of PBDGE on electrochemical processes and the coordination effect with other additives during electrodeposition were investigated through electrochemical experiments. The electroplating results prove that PBDGE can make the copper coating in TH more uniform under certain electroplating conditions.

### RESULTS AND DISCUSSION

The polymerization process of pyrrole and BDGE is shown in Figure 2. Glycidyl ether ring-opening reaction takes place under alkaline conditions31 and then undergoes polymerization with pyrrole. During polymerization, glycidyl ether polymerizes with pyrrole; then, the self-polymerization reaction occurs as well. Because the chain grows through a similar reaction for both pyrrole and BDGE, a random copolymer comprising pyrrole and BDGE is formed.

The structure of this copolymer was investigated through Fourier transform infrared (FTIR) spectroscopy. Figure 3 illustrates the FTIR spectra of pyrrole (curve a), BDGE (curve b), and PBDGE (curve c) generated by 6 h of reaction.

![Figure 2](https://example.com/f2.png)

**Figure 2.** Synthetic reaction of copolymers of pyrrole and 1,4-butanediol diglycidyl ether.

![Figure 3](https://example.com/f3.png)

**Figure 3.** IR spectra of pyrrole (a), 1,4-butanediol diglycidyl ether (b), and poly(pyrrole-co-1,4-butanediol diglycidyl ether) (c).
between pyrrole and BDGE. The epoxide characteristic peak (912 cm\(^{-1}\)) of the reactant BDGE completely disappears in the spectrum of PBDGE, which means that BDGE undergoes a ring-opening reaction.\(^7\) The characteristic peak enhancement of the hydroxyl group at 3700 cm\(^{-1}\) in the PBDGE curve also supports the occurrence of an open-loop reaction in the epoxy group.\(^32\) In addition, there is a characteristic peak of the copolymer product at 1356 cm\(^{-1}\) implying the formation of C–N, which is absent in the spectra pyrrole (curve a) and BDGE (curve b).\(^33\)

Table 1 lists the number-average molecular weight (\(M_n\)), weight-average molecular weight (\(M_w\)), and polydispersity of PBDGE. \(M_n\) and \(M_w\) of PBDGE are 2637 and 3390, respectively. The high purity of PBDGE is implied by the value of 1.28 for polydispersity.

The influences of PBDGE on the potential dynamic polarization behavior in the case of copper electrodeposition in the base electrolyte are shown in Figure 4a. In electrochemical experiments, the transfer rates of reactants at the center and mouth of the TH are simulated by different rotation speeds of the working electrode (WE).\(^10\) The low (100 rpm) and high (1500 rpm) rotation speeds correspond to the center and mouth of the TH, respectively. As detailed in Figure 4a, the polarization of the samples with strong convection is more intense than the ones with weak convection because the forced convection dominates the transfer of reactants in the cathode electrochemical reaction with the absence of PBDGE.\(^34\) PBDGE caused polarization in the electrolyte because the cathode potential dropped immediately when 20 mg L\(^{-1}\) PBDGE was introduced. Moreover, the high rotation speed displays a significantly stronger electrode working polarization than the one at the low rotation speed. In other words, PBDGE is able to enhance the inhibition of copper deposition at a higher rotation speed, which implies that the copper deposition rate at TH center is higher than the one at the TH mouth.

The influence of PBDGE on TH plating was studied at low rotation speeds (100 rpm) and high rotation speeds (1500 rpm) at 2 A dm\(^{-2}\) with the GMs, as illustrated in Figure 4b. The potential difference at different rotating speeds \(\Delta \eta_{1}\) defined by \(\Delta \eta_{1} = \eta_{100\text{rpm}} - \eta_{1500\text{rpm}}\) is used to evaluate the inhibitive performance of copper deposition.\(^12\) With the addition of 500 mg L\(^{-1}\) PEG-10 000 at 300 s, the cathodic potentials dropped rapidly. This drop is due to the electrode polarization by PEG. A difference in the potential decrement \(\Delta \eta_{1}\) is observed between the two tested groups. In the presence of PEG, 1 mg L\(^{-1}\) SPS weakened the polarization and the \(\Delta \eta_{1}\) value changed from negative to positive (\(\Delta \eta_{1} = +1.1.6\) mV). This trend continued until the next addition of PBDGE in the plating solution, which confirms that the acidic electrolytes are brighter (SPS)-dominated system. The cathode polarization was enhanced when 20 mg L\(^{-1}\) PBDGE was added at 1800 s. As displayed in Figure 4b, the value of \(\Delta \eta_{1}\) is higher than that of \(\Delta \eta_{2}\). This result represents that the high transfer rate suppresses the copper electrodeposition at the mouth of TH.\(^12,21\) In summary, the adsorption of PBDGE on the cathode is positively correlated with the convective intensity; meanwhile, stronger convection leads to greater overpotential. When PEG and Cl\(^{-}\) are both in the bath, the copolymer PBDGE interestingly inhibits the SPS accelerating activity for copper electrodeposition.

Cyclic voltammetry (CV) tests were performed to investigate the interactive behavior of the additives in copper deposition (Figure 5). The amount of electrodeposited copper on the cathode under different conditions is listed in Table 2. As illustrated in Figure 5a, the addition of PBDGE in the plating bath caused the copper stripping peak to become smaller, indicating that PBDGE enhances cathodic polarization. The addition of Cl\(^{-}\) at the existence of PBDGE led to a more negative shift of deposition potentials than in the case of PBDGE alone. The corresponding results are also found in the high convection condition (Figure 5b). Therefore, the CV tests prove that Cl\(^{-}\) can be in conjunction with PBDGE to inhibit copper electrodeposition. This synergistic effect is effective both at weak and strong convection conditions.

The CV results in Figure 5 reveal that PBDGE can inhibit copper electrodeposition without Cl\(^{-}\) in the plating bath. The amount of electrodeposited copper at 1500 rpm is less than that at 100 rpm, which indicates that strong convection is
beneficial to the inhibition of copper electrodeposition by PBDGE. These facts are in accordance with the results of linear sweep voltammetry (LSV) and GMs discussed above. When PEG was added into the electrolyte, the inhibitory effect of PBDGE was obviously weakened (Figure 5b), which indicates the competitive adsorption between PEG and PBDGE. As shown in Figure 5, the addition of SPS in the presence of other additives can increase the amount of copper electrodeposition, indicating that SPS has the effect of depolarization in the cathode.

As listed in Table 2, with the addition of PBDGE, the amount of electroplated copper at 100 rpm is more than that at 1500 rpm. This trend is inverted in the case of VMS. With the addition of SPS, a greater increase in the amount of electrodeposited copper occurred at 100 rpm, indicating that the depolarization effect of SPS is stronger under weak convection. This result illustrates that the additive system of PEG + Cl⁻ + SPS + PBDGE + Cl⁻ can effectively inhibit the copper electrodeposition at the mouth and causes the copper thickness to increase at the center of TH.

The compositions of electroplating baths with and without leveler are shown in Table 3. The corresponding TH cross sections are illustrated in Figure 6. The TP value is 54.5% when the leveler is absent, and the TP value can increase to 72.4% with JGB (Figure 6b). Notably, the TP value can be further increased to 90% with the addition of PBDGE. The copper thickness of the TH center increased from 15 to 24 µm (Figure 6c). The TH electroplating experiments show that PBDGE has a strong inhibition of copper electrodeposition on the TH mouth. As a result, the current density distribution on the whole hole surface is effectively improved because of the inclusion of PBDGE.23,35

According to the frontier molecular orbital theory, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the keys to determine the chemical reactivity of a system.36 The simulated HOMO and LUMO of PBDGE are given in Figure 7. Generally, $E_{\text{HOMO}}$ is related to the electron-donating ability and $E_{\text{LUMO}}$ is closely interrelated to the ability of molecules to accept electrons.37,38 The energy gap ($\Delta E$) should be calculated by $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$. The adsorption capacity of organic molecules on the metal surface increases with the decreasing $E_{\text{LUMO}}$ or increasing $E_{\text{HOMO}}$.39,40 Generally, $\Delta E$ is relevant to the chemical stability of the leveler and could be used to evaluate the adsorption ability. As shown in Figure 7, $E_{\text{HOMO}}$ of PBDGE is ~6.070 eV, which is near $E_{\text{HOMO}}$ of JGB (~5.689 eV).18 $E_{\text{LUMO}}$ of PBDGE is ~0.114 eV, which is much less than $E_{\text{LUMO}}$ of JGB (~3.635 eV).18 These calculated energy levels support the fact that PBDGE is an effective leveler. It is also observed in Figure 7 that the LUMO and HOMO of PBDGE molecules are mainly concentrated on the pyrrole ring of PBDGE, which implies that the pyrrole ring of PBDGE is in the active position of adsorption with the copper surface.

Molecular dynamics simulations were used to analyze the adsorption behaviors of PBDGE at the Cu(111) crystal surface.41 Figure 8 shows that the pyrrole rings of PBDGE are adsorbed on the copper surface in the final equilibrium configuration. The calculated value of $E_{\text{binding}}$ of PBDGE is ~150.662 KJ/mol, which is larger than that of $E_{\text{binding}}$ of JGB.18 A high $E_{\text{binding}}$ indicates the strong adsorption capacity between PBDGE and copper surface.32,45 The electrostatic effect between PBDGE and copper surface governs the competitive adsorption of additives. PBDGE's adsorption results in a reduction in the area of copper exposed from the cathode, which affects the copper electrodeposition. This simulation supports the fact that PBDGE as a discovered leveler is as effective as the common leveler JGB.23

### CONCLUSIONS

In this article, a leveler, PBDGE, employed for TH electroplating was synthesized and analyzed. An excellent TH plating sample with the TP value of 90% with the increased copper thickness at the center of TH was obtained. The optimized copper plating formula is composed of 60 mg L⁻¹ Cl⁻, 500 mg L⁻¹ PEG, 1 mg L⁻¹ SPS, and 20 mg L⁻¹ PBDGE. The addition of PBDGE increases the cathodic polarization and inhibits the copper electrodeposition. The inhibitory effect of PBDGE on the copper mouth is stronger with the existence of all the additives, which is beneficial to obtain the uniform...
coating in electroplating. On the other hand, it is found that \( \text{Cl}^- \) has a synergistic effect with PBDGE, which can enhance the inhibition of PBDGE. This is of vital importance to the through-hole interconnection of PCB for electronic information products that are being developed for the purpose of miniaturization, integration, and portability. Simulation results show that the pyrrole ring on PBDGE is the active position of copper surface adsorption. Additionally, the simulation shows that PBDGE has a strong adsorption tendency on the copper surface, which can reduce the surface area of exposed copper and inhibit copper electrodeposition.

### METHODS

The PBDGE copolymer was synthesized on the basis of the amine glycidyl reaction using pyrrole (99.7%, Shanghai Aladdin Co., Ltd.) and 1,4-butanediol diglycidyl ether (60%, Shanghai Aladdin Co., Ltd.) as reactants. Pyrrole (5 mol L\(^{-1}\)) and BDGE (5 mol L\(^{-1}\)) were added into 1 mol L\(^{-1}\) KOH in a round-bottom flask under nitrogen protection. This mixture was stirred at 300 rpm for 6 h and 338 K. After the reaction, the solvent in the mixture was removed by rotary evaporation and dried under vacuum at 10\(^{-2}\) mbar. Moreover, this product can be pure PBDGE by removing the unreacted reactants by washing with tetrahydrofuran solution several times, and then evaporating the residual tetrahydrogen peroxide by rotary evaporation.

Electrochemical behaviors of PBDGE were characterized by linear sweep voltammetry (LSV), galvanostatic measurements (GMs), and cyclic voltammetry (CV) tests using platinum rotating disk electrode (Pt-RDE) operated at 100 and 1500 rpm. All of the electrochemical experiments were conducted in a 250 mL glass beaker including 200 mL of electroplating solution by an Autolab (PGSTAT302N, Metrohm) electrochemical workstation with a conventional three-electrode system. The electroplating solution temperature was kept at 298 K during electrochemical experiments. The working electrode (WE) was a platinum rotating disk electrode (Pt-RDE) with a diameter of 5 mm. The counter electrode (CE) was a copper rod and the reference electrode (RE) was a saturated mercury sulfate electrode (SSE). The LSV polar-
ization plots were recorded with a negative-going sweep from an open-circuit potential to $-0.9 \, \text{V}$ vs SSE. The current density of GMs was set up at $2 \, \text{A cm}^{-2}$ at 100 and 1500 rpm. The electrode scanning potentials of CV tests were measured to be from $-0.685$ to $1.2 \, \text{V}$.

Printed circuit boards with several rows of through-holes are used to make test boards, and the diameter and height of these THs are 0.25 and 1.6 mm, respectively. These test boards deposited conductive copper by electroless copper before electroplating. The anode used for electroplating is a phosphorus copper anode. The test boards were plated at a current density of $2 \, \text{A dm}^{-2}$ for 70 min in 1.5 L Haring cell at 298 K. Air bubble agitation continuously flowed out from the bottom of the Haring cell at a flow rate of $2.5 \, \text{L min}^{-1}$ to provide sufficient convection. Virgin make-up solution (VMS) consisted of $75 \, \text{g L}^{-1} \, \text{CuSO}_4 \cdot \text{SH}_2\text{O}$ and $240 \, \text{g L}^{-1} \, \text{H}_2\text{SO}_4$. SPS was used as the accelerator, PEG ($M_w = 10000$) was the inhibitor, while PBDGE was added as the leveler.

Quantum chemical calculations were performed by Gaussian 09. Geometry optimizations were carried out by density functional theory (DFT) using B3LYP functional with the 6-311G+(d,p) basis set. The frontier molecular orbital energies and energy gap of PBDGE were calculated and considered. These parameters were used to further elaborate the mechanism of interaction between PBDGE and copper surface.

The adsorption model between PBDGE and the Cu(111) surface was studied by employing the forcite module in Material Studio software. The MD simulations were performed under the constraints of 298 K, NVT ensemble, and COMPASS force field. MD simulations of the interaction between PBDGE and the copper crystal were performed in a simulation box ($3.10 \times 3.10 \times 5.99 \, \text{nm}^3$). There is a copolymer PBDGE molecule, 500 water molecules, and seven layers of copper atoms neatly arranged at the bottom. The interaction energy $E_{\text{Cu-PBDGE}}$ between the copper atoms and PBDGE was calculated by eq 2.

$$E_{\text{Cu-PBDGE}} = E_{\text{complex}} - E_{\text{Cu}} - E_{\text{PBDGE}} \tag{2}$$

$E_{\text{complex}}$ is the total energy of copper, PBDGE, and the interaction of copper and PBDGE; $E_{\text{Cu}}$ and $E_{\text{PBDGE}}$ are the energies of the copper crystal and free PBDGE, respectively. Also, the negative value of the interaction energy is the binding energy.

The molecular structure of purified copolymer was characterized by Fourier transform infrared (FTIR) spectroscopy. The average molecular weight was provided by gel permeation chromatography (GPC) tests. FTIR tests were carried out in a Nicolet 6700 spectroscope (Thermo Scientific) in transmission mode. The spectra were obtained at a wavelength of 4000~5000 cm$^{-1}$. GPC measurements were performed in Waters 2695 configured with an RI detector.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Dow, W.-P.; Li, C.-C.; Lin, M.-W.; Su, G.-W.; Huang, C.-C. Copper Fill of Microvia Using a Thiol-Modified Cu Seed Layer and Various Levelers. J. Electrochem. Soc. 2009, 156, D314–D320.

(2) Zan, L. X.; Liu, Z. H.; Yang, Z. P.; Wang, Z. L. A Synergy Effect of 2-MBT and PE-3650 on the Bottom-Up Filling in Electroless Copper Plating. Electrochem. Solid-State Lett. 2011, 14, D107–D109.

(3) Liu, X.; Chen, Y.; Yan, D.; Jin, X.; Zeng, Y.; Zhang, D.; Liu, Z.; He, W.; Chen, Q.; Miao, H.; Zhou, J. Enhancing adhesion performance of sputtering Ti/Cu film on pretreated composite prepg for stacking structure of IC substrates. Composites, Part B 2019, 158, 400–405.

(4) Chen, Y.; Yan, D.; Jin, X.; Zeng, Y.; Zhang, D.; Liu, Z.; He, W.; Wang, S.; Wang, Z.; Liu, Y.; Zhang, W.; Huang, Y. Solvent-dependent ultrasonic surface treatment on morphological reconstruction of CuO particles for copper electrodeposition. Appl. Surf. Sci. 2019, 491, 206–215.

(5) Chen, Y.; Chen, Y.; Wang, J.; Zhu, K.; Jia, L.; Wang, S.; He, W.; Chen, Q.; Miao, H.; Zhou, J. Copper Through-Hole Electroplating Process. J. Electrochem. Soc. 1989, 136, 756–767.

(6) Zan, L. X.; Liu, Z. H.; Yang, Z. P.; Wang, Z. L. A Synergy Effect of 2-MBT and PE-3650 on the Bottom-Up Filling in Electroless Copper Plating. Electrochem. Solid-State Lett. 2011, 14, D107–D109.

(7) Yang, E. K.; Romankiw, L. T. Fundamental Study of Acid Copper Through-Hole Electroplating Process. J. Electrochem. Soc. 2019, 166, 756–767.

(8) Dow, W.-P.; Chen, H.-H.; Yen, M.-Y.; Chen, W.-H.; Hsu, K.-H.; Chang, P.-Y.; Ishizuka, H.; Sakagawa, N.; Kimizuka, R. Through-Hole Filling by Copper Electroplating. J. Electrochem. Soc. 2008, 155, D750–D757.

(9) Liu, X.; Chen, Y.; Yan, D.; Jin, X.; Zeng, Y.; Zhang, D.; Liu, Z.; He, W.; Chen, Q.; Miao, H.; Zhou, J. Enhancing adhesion performance of sputtering Ti/Cu film on pretreated composite prepg for stacking structure of IC substrates. Composites, Part B 2019, 158, 400–405.

(10) Chen, Y.; Yan, D.; Jin, X.; Zeng, Y.; Zhang, D.; Liu, Z.; He, W.; Wang, S.; Wang, Z.; Liu, Y.; Zhang, W.; Huang, Y. Solvent-dependent ultrasonic surface treatment on morphological reconstruction of CuO particles for copper electrodeposition. Appl. Surf. Sci. 2019, 491, 206–215.
(10) Dow, W.-P.; Huang, H.-S.; Yen, M.-Y.; Huang, H.-C. Influence of Convection-Dependent Adsorption of Additives on Microvia Filling by Copper Electroplating. J. Electrochem. Soc. 2005, 152, C425−C434.

(11) Wang, S.; Tian, Y. H.; Wang, C. X.; Hang, C. J.; Zhang, H.; Huang, Y.; Zheng, Z. One-Step Fabrication of Copper Nanopillar Array-Filled AAO Films by Pulse Electrodeposition for Anisotropic Thermal Conductive Interconnectors. ACS Omega 2019, 4, 6092−6096.

(12) Dow, W.-P.; Liu, C.-W. Evaluating the filling performance of a copper plating formula using a simple galvanostat method. J. Electrochem. Soc. 2006, 153, C190−C194.

(13) Taephasitphongse, P.; Cao, Y.; West, A. C. Electrochemical and fill studies of a multicomponent additive package for copper deposition. J. Electrochem. Soc. 2001, 148, C492−C497.

(14) Kondo, K.; Matsumoto, T.; Watanabe, K. Role of additives for copper damascene electrodeposition experimental study on inhibition and acceleration effects. J. Electrochem. Soc. 2004, 151, C230−C235.

(15) Hasegawa, M.; Negishi, Y.; Nakashima, T.; Osaka, T. Effects of Additives on Copper Electrodeposition in Submicrometer Trenches. J. Electrochem. Soc. 2005, 152, C221−C228.

(16) Walker, M. L.; Richter, L. J.; Moffat, T. P. Potential Dependence of Competitive Adsorption of PEG, Cl[super −], and SPS/MPS on Cu. J. Electrochem. Soc. 2007, 154, D277−D282.

(17) Wang, C.; An, M. Z.; Yang, P. X.; Zhang, J. Q. Prediction of a new leveler (N-butyl-methyl piperidinium bromide) for through-hole electroplating using molecular dynamics simulations. Electrochim. Commun. 2012, 18, 104−107.

(18) Lai, Z. Q.; Wang, S. X.; Wang, C.; Hong, Y.; Zhou, G. Y.; Chen, Y. M.; He, W.; Peng, Y. Q.; Xiao, D. A comparison of typical additives for copper electroplating based on theoretical computation. Comput. Mater. Sci. 2018, 147, 95−102.

(19) Dow, W.-P.; Yen, M.-Y.; Chou, C.-W.; Liu, C.-W.; Yang, W.-H.; Chen, C.-H. Practical monitoring of filling performance in a copper plating bath. Electrochem. Solid-State Lett. 2006, 9, C134−C137.

(20) Zhu, K.; Wang, C.; Wang, J.; Hong, Y.; Chen, Y.; He, W.; Zhou, J.; Miao, H.; Chen, Q. Convection-Dependent Competitive Adsorption between SPS and EO/PO on Copper Surface for Accelerating Trench Filling. J. Electrochem. Soc. 2019, 166, D93−D98.

(21) Dow, W.-P.; Li, C.-C.; Su, Y.-C.; Chen, S.-P.; Huang, C.-C.; Lee, C.; Hsu, B.; Hsu, S. Microvia filling by copper electroplating using diazine black as a leveler. Electrochim. Acta 2009, 54, S594−S591.

(22) Chen, B.; Xu, J.; Wang, L.; Song, L.; Wu, S. Synthesis of Quaternary Ammonium Salts Based on Diketopyrrolopyrroles Skeletons and Their Applications in Copper Electroplating. ACS Appl. Mater. Interfaces 2017, 9, 7793−7803.

(23) Lühl, O.; Van Hoof, C.; Raythooren, W.; Celis, J.-P. Filling of microvia with an aspect ratio of 5 by copper electrodeposition. Electrochim. Acta 2009, 54, 2504−2508.

(24) Tang, M.; Zhang, S.; Qiang, Y.; Chen, S.; Luo, L.; Gao, J.; Feng, L.; Qin, Z. 4,6-Dimethyl-2-mercaptoimidazoline as a potential leveler for microvia filling with electroplating copper. RSC Adv. 2017, 7, 40342−40353.

(25) Kim, S.-K.; Josell, D.; Moffat, T. P. Cationic Surfactants for the control of overfill bumps in Cu superfilling. J. Electrochem. Soc. 2006, 153, C826−C833.

(26) Broekmann, P.; Fluegel, A.; Emmet, C.; Arnold, M.; Roeger-Goeft, C.; Wagner, A.; Haï, N. T. M.; Mayer, D. Classification of suppressor additives based on synergistic and antagonistic ensemble effects. Electrochim. Acta 2011, 56, 4724−4734.

(27) Hatch, J. J.; Willey, M. J.; Gewirth, A. I. Influence of Aromatic Functionality on Quaternary Ammonium Levelers for Cu Plating. J. Electrochem. Soc. 2011, 158, D323−D329.

(28) Hai, N. T. M.; Furrer, J.; Stricker, F.; Huyhn, T. M. T.; Gjorloski, I.; Luedi, N.; Brunner, T.; Weiss, F.; Fluegel, A.; Arnold, M.; Chang, I.; Mayer, D.; Broekmann, P. Polyvinylpyrrolidones (PVPs): Switchable Leveler Additives for Damascene Applications. J. Electrochem. Soc. 2013, 160, D3116−D3125.