Influence of Convection-Dependent Adsorption of Additives on Microvia Filling by Copper Electroplating

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Influences of forced convection during acid copper electroplating on microvia fill of printed circuit boards were studied. The plating formula was composed of polyethylene glycol (PEG), chloride ion, 3-mercaptop-1-propanesulfonate, and Janus green B (JGB). The filling performances under various plating conditions were examined with scanning electron microscopy and optical microscopy. Chemical and physical interactions between these additives and fluid dynamics were characterized by cyclic linear sweep voltammetry, steady-state current-potential measurements, linear sweep voltammetry, and galvanostatic measurements using different rotation speeds of working electrode. Experimental results indicated that the potential-dependent adsorption of chloride ion on the copper surface determined and governed the electrochemical effect of these organic additives on the cathode, resulting in a convection-dependent adsorption of inhibiting reagents and an asymmetrical fill of copper deposit in the microvias. A synergistic inhibition effect on the copper deposition caused by a composite suppressor composed of PEG, Cu²⁺, Cl⁻, and JGB was demonstrated. The dominance of the competitive adsorption between the accelerator and the composite suppressor was shown to depend significantly on the chloride ion concentration and on the forced convection.

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In this work, a typical leveler (i.e., JGB) was chosen as the model additive. An attempt was made to elucidate the JGBs electrochemical and adsorptive behaviors and to correlate these behaviors with the filling performance of the plating formula. Besides, this work demonstrated that there was a synergistic interaction between the suppressor (i.e., PEG) and the leveler (i.e., JGB), which significantly redoubled the inhibition effect on copper deposition compared to that of individual reagents, and thus redounded to the filling performance. This synergistic inhibition effect between PEG and JGB was demonstrated to be related with forced convection. Therefore, the improvement of filling performance following the addition of the leveler could be reasonably explained if the impingement of forced convection acting at the via opening and the board surface was much stronger than at the bottom. This work further clarified the mechanism of microvia fill, in which the accelerator was predominant at the bottom of the microvia due to weak convection and the suppressor and the leveler were synergistically predominant at the via opening and at the board surface owing to strong convection. Once the synergy between suppression and acceleration deviated from balance, conformal deposition was obtained. Sometimes an oblique copper plane at the top of the filled microvia was obtained due to the unidirectional flow of the plating solution. Experimental results indicated that PEG and JGB could interact and give rise to a synergistic inhibition effect on copper electrodeposition. This synergy of PEG and JGB was convection-dependent.

Experimental

The preparations and pretreatments of the PCB fragments with various via diameters have been described in detail elsewhere.8,10

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The procedures of the filling plating have also been reported in previous works.\textsuperscript{8,10} Constant agitation was performed by a continuous flow of air bubbles during electroplating to ensure good mass transfer. The rectangular PCB fragment was placed vertically at the center of the plating bath. Small rising air bubbles formed two rows from the downside of the PCB fragment and thus created a continual tangential fluid flow along the PCB fragment’s surface. The continuous fluid motion on the board surface almost always flowed in one direction. Therefore, the direction of the stream line on the board surface was fixed during electroplating. The plating bath was illustrated in detail elsewhere.\textsuperscript{10}

The composition of standard electrolyte used in all filling tests was 0.88 M CuSO\textsubscript{4}·5H\textsubscript{2}O (Riedel-de Haën, ACS) and 0.54 M H\textsubscript{2}SO\textsubscript{4} (Merk, 96%, Ultrapure). The additives, MPS (Aldrich), JGB (Aldrich), and PEG with a molecular weight of 8000 (Fluka), and chloride ion (i.e., NaCl) (Fisher, Certified ACS), were added consecutively to the plating solution. The temperature of the plating solution during electroplating was maintained at 25°C. The filling performance of different plating formulas was examined with scanning electron microscopy (SEM, Hitachi S-3500N) for a top view of the microvia and with optical microscopy (OM) for a cross-sectional view of the microvia.

The electrochemical and inhibitive behaviors of the leveler were characterized with cyclic linear sweep voltammetry (CLSV) using different rotation speeds of the working electrode (WE). All CLSV measurements were performed in a glass vessel containing 100 mL of electrolyte solution and using a PGSTAT30 (AUTOLAB) potentiostat with a three-electrode cell. A platinum rotating disk electrode (Pt-RDE) with a diameter of 3 mm was employed as the WE. A small platinum foil was chosen as a counter electrode (CE) and a saturated mercurous sulfate electrode (SSE) served as a reference electrode (RE). The CLSV was carried out by a negative-going sweep from open circuit potential (OCP) to −0.9 V vs. SSE, followed by a positive-going sweep from −0.9 V vs. SSE to OCP.

To simulate the fluid motion around the PCB, two rotation speeds of WE were chosen. One was fixed at 150 rpm to simulate the fluid motion at the via bottom. The other was set at 2500 rpm to simulate the fluid motion at the board surface. The scan rate was 1 mV/s for all CLSV measurements. Before each CLSV measurement, a thin copper layer of 500 nm was predeposited onto the Pt-RDE in a predeposition bath, containing only 0.06 M CuSO\textsubscript{4}·5H\textsubscript{2}O (Riedel-de Haën, ACS) and 0.9 M H\textsubscript{2}SO\textsubscript{4} (Merk, 96%, Ultrapure). The test electrolyte was first purged with nitrogen for 1 h before CLSV measurement in order to remove the dissolved oxygen from the solution.

To emphasize the effects and interactions of the additives on the copper electrodeposition, CLSV measurements were carried out in a base electrolyte composed of 0.06 M CuSO\textsubscript{4}·5H\textsubscript{2}O and 0.9 M H\textsubscript{2}SO\textsubscript{4}. Low cupric ion concentration and high H\textsubscript{2}SO\textsubscript{4} concentration (i.e., supporting electrolyte) could markedly enhance the resolution and sensitivity of current density variation in the CLSV measurements, because the resistance of the base electrolyte was decreased and the migration current of cupric ion was reduced. Based on this analysis condition, significant polarization behaviors of these additives relative to an additive-free solution were obtained, which was greatly helpful in explaining the causal relationships between the chemical interaction and the fluid dynamics.

The influence of the chloride ion concentration on PEG adsorption at different forced convection levels and the potential-dependent adsorption of chloride ions on the copper surface were characterized by steady-state current-potential measurements. The base electrolyte prepared for the measurement was composed of 0.88 M CuSO\textsubscript{4}·5H\textsubscript{2}O and 0.54 M H\textsubscript{2}SO\textsubscript{4}, which was the same composition as that used for practical plating. The PEG concentration was fixed at 200 ppm for all measurements. Two chloride ion concentrations, 10 and 90 ppm, were chosen for comparison. To demonstrate that the suppression effect of the inhibitor (i.e., PEG + JGB) was sensitive to the chloride ion concentration, a linear sweep voltammetry (LSV) was carried out by using a practical plating solution. The rotation speed of the WE was 400 rpm during the LSV measurement. The scan rate and range were the same as those of CLSV.

To further explore the competitive adsorption among these additives, several galvanostatic measurements (GMs) were carried out in practical plating solutions with various formulas. The current density adopted in the GMs was 18 A/ft\textsuperscript{2} (ASF = 19.4 mA/cm\textsuperscript{2}) which was the same as the filling plating condition. Also, two rotation speeds, 150 and 2500 rpm, were chosen to simulate the fluid motion at the bottom of the microvia and at the board surface, respectively. The total time for each GM was 70 min, which was equal to the practical plating time. The measurements, pretreatments, and procedures were described in detail elsewhere.\textsuperscript{11}

Results

Filling plating.— A previous work\textsuperscript{10} has shown that superfill was obtained from a plating formula with 200 ppm PEG, 90 ppm Cl\textsuperscript{−}, and 0.3 ppm MPS. When the MPS concentration was increased to 3 ppm, and the PEG and Cl\textsuperscript{−} concentrations were still fixed at 200 and 90 ppm, respectively, conformal deposition was obtained. Therefore, if accumulation of the accelerator in the microvia is a crucial factor for the performance of superfill,\textsuperscript{12,18} a premise that a strong inhibition effect has to simultaneously function at the via opening and at the board surface must be established. Otherwise, cathodic current does not preferentially work at the bottom of the microvia.

Interestingly, the conformal deposition caused by the unworkable plating formula (i.e., 200 ppm PEG + 90 ppm Cl\textsuperscript{−} + 3 ppm MPS) could be turned into a superfill after JGB was used along with PEG and MPS. Figure 2 shows the SEM images of several microvias of various diameters formed on the same PCB fragment after electroplating was performed in a plating solution with 200 ppm PEG, 90 ppm Cl\textsuperscript{−}, 3 ppm MPS, and 1 ppm JGB. Figure 3 shows the corresponding cross-sectional views of the microvias. According to the direction of fluid motion, Fig. 4 illustrates two specific locations near the microvia opening, namely, A and B. The direction of the fluid motion is defined within area A is essentially opposite to the direction of fluid motion, whereas the direction of the surface defined within area B is essentially parallel to the direction of fluid motion. Apparently, the small vias, as shown in Fig. 2i, were fully filled by copper deposit and exhibited superfilling behavior, while as to the large

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{molecularstructures.png}
\caption{Molecular structures of typical levelers: (A) Janus Green B (JGB), and (B) Diazine black (DB).}
\end{figure}
vias, a large cavity was still seen in Fig. 2a-e, 3e, and f due to insufficient plating time. As to the medium vias, a small cavity near area A still existed, as shown in Fig. 2f-h, 3c, and d. Notably, the top planes of the large vias were oblique after the filling deposition, as shown in Fig. 2a-d, 3e, and f. The deposition rate at area A was lower than at area B, indicating that the deposition rate was convection-dependent. Namely, less copper was deposited at the place where the impact of fluid flow was strong. Actually, a plating formula without a leveler but with other components, the same as the case shown in Fig. 2, resulted in a conformal deposition; namely, copper was isotropically deposited at the bottom and side-wall of the microvia and evenly deposited at the board surface, respectively. Hence, the uneven deposition around the perimeter of the microvia was not only dependent on the direction of fluid motion but also on the effect of the leveler. The SEM images shown in Fig. 2 identified that a number of small nodules were located on the copper deposit within area B, whereas a number of small pinholes were located on the copper deposit within area A. These findings imply that certain additives with strong inhibition effect preferred to work on the surface of area A. Certain additives with strong acceleration effect preferred to work on the surface of area B. This selective action of these additives on the copper deposition was associated with the impact of fluid motion.

When the JGB concentration was increased to 3 ppm, the entire copper surface deposited on the board surface, including the top areas of the filled microvias, as shown in Fig. 5, was a flat plane, regardless of via diameter. Under this plating condition, the copper deposition around the via perimeter was independent of the direction of fluid motion. Additionally, the feature of the superfill, hemispheric bump on the via top, was not formed, indicating that as the JGB concentration exceeded a certain value, the leveling effect could thoroughly function at the board surface by means of the strong tangential fluid motion.

As can be seen from the SEM images shown in Fig. 2, the surface morphology of the copper deposit located at the top area of the filled microvia differed from the surface morphology at the other places on the board surface. The surface morphology at the top area of the filled microvia was fine and smooth, whereas it was rough and bumpy at the other places. This phenomenon was also found in the case where the JGB concentration was 3 ppm. The SEM images in Fig. 6 show that two different surface morphologies of the copper deposit existed on the same PCB fragment after the filling plating terminated. The concentration distribution of various additives in the bulk solution was uniform during electroplating because of the strong agitation by air bubbles. Therefore, the location-dependent surface morphologies should result from the locally different composition of additives. The copper surface located at the top area of the filled microvia was elevated from the bottom of the microvia due to the behavior of bottom-up fill. Hence, the fine-grained copper deposit shown in Fig. 6c demonstrated that the composition acting at

**Figure 2.** Typical SEM images of microvias after electroplating. Plating formula is composed of 0.88 M CuSO$_4$$\cdot$5H$_2$O + 0.54 M H$_2$SO$_4$ + 200 ppm PEG + 90 ppm Cl$^-$ + 3 ppm MPS + 1 ppm JGB. Via diameters are (a) 165, (b) 155, (c) 142, (d) 137, (e) 119, (f) 112, (g) 104, (h) 85, and (i) 68 μm. Via depth is 55 μm. White arrows indicate the direction of fluid motion during electroplating. Except for (c) and (d), all the SEM specimens are inclined at 30°. SEM magnification is 600-fold.
the bottom of the microvia was different from that acting on the board surface during electroplating; that is, the composition of the additives adsorbed on the copper surface were convection- and location-dependent. In the microvia, the fluid velocity is slower compared with the outside bulk velocity, such that the shear force of the fluid acting on the copper surface at the via bottom is weak. This scenario is beneficial to the action of the accelerator.\textsuperscript{11} The shear force of the fluid strongly impacts on the board surface, which is beneficial to the action of the suppressor.\textsuperscript{11} These behaviors are characterized by the following CLSV and GMs and are in agreement with the previous work.\textsuperscript{11}

**CLSV of JGB.**—Figure 7A shows CLSV curves of the suppressing reagents measured on a copper electrode with a rotation speed of 150 rpm. The inhibition effect of 200 ppm PEG + 90 ppm Cl\textsuperscript{−} was considerably stronger than that of 3 ppm JGB. The inhibition effect of JGB on copper deposition obviously depended on the applied potential of the WE. When the potential of the WE was higher than ca. −0.65 V, JGB immediately lost its inhibition effect and inversely exhibited a slight depolarization effect compared with the additive-free electrolyte. This abrupt depolarization effect of JGB at a particular potential can be attributed to the desorption of chloride ion\textsuperscript{~}\textsuperscript{!}see Discussion\textsuperscript{~}\textsuperscript{!}. When the potential of WE was higher than −0.65 V, the incidental chloride ion in JGB, which is a catalyst for Cu\textsuperscript{2+} reduction,\textsuperscript{20,21} would dominate the copper deposition rate and thereupon result in a depolarization effect on the WE.

When the JGB concentration was increased to 3 ppm, as shown in Fig. 7A, its inhibition effect on copper deposition was still weaker than that of 200 ppm PEG + 90 ppm Cl\textsuperscript{−}. When the rotation speed of the WE was raised to 2500 rpm, the inhibition effect of JGB was enhanced, as shown in Fig. 7B, but the characteristics of the CLSV curves were still similar to those measured at 150 rpm. The enhanced inhibition effect achieved by speeding up forced convection was attributed to the diffusion-limited transfer of JGB\textsuperscript{6,15,17} and the convective transport of Cl\textsuperscript{−}\textsuperscript{~}\textsuperscript{!}see Discussion\textsuperscript{~}\textsuperscript{!}.

**CLSV of PEG + Cl\textsuperscript{−} + JGB.**—When PEG, Cl\textsuperscript{−}, and JGB were concurrently present in the electrolyte, a strong inhibition effect compared to that of PEG + Cl\textsuperscript{−} was obtained in Fig. 8A. The inhibitive extent and performance of the mixed additives were markedly greater than that of PEG + Cl\textsuperscript{−}. Apparently, the window of the hysteresis loop became wider compared with Fig. 7, and the positive-going curve of PEG + Cl\textsuperscript{−} + JGB almost superposed that of PEG + Cl\textsuperscript{−}. These phenomena indicate that the combination of PEG-Cl\textsuperscript{−}
and JGB can result in a synergistic inhibition effect on the copper deposition. The synergistic inhibition effect arises from a composite suppressor composed of PEG, Cl\(^-\), and JGB.

The synergistic inhibition effect caused by the composite suppressor became more conspicuous after the rotation speed of the WE was increased to 2500 rpm, particularly for the case in which 3 ppm JGB was applied. As can be seen from Fig. 8B, an extremely strong suppression of copper deposition was obtained from the electrolyte containing 200 ppm PEG, 90 ppm Cl\(^-\), and 3 ppm JGB at the WE rotation speed of 2500 rpm. Under this condition, the positive-going curve of PEG + Cl\(^-\) + JGB significantly deviated from that of PEG + Cl\(^-\), which is attributed to the rapid replenishment of chloride ion and JGB.

However, if the JGB concentration was 1 ppm, the positive-going curve of the composite suppressor almost entirely superposed the polarization curve of PEG + Cl\(^-\), indicating that high JGB concentration and strong forced convection were significant factors in maintaining the synergistic inhibition effect.

**CLSV of PEG + Cl\(^-\) + JGB + MPS.**—Figure 9 shows that JGB did not have an inhibition effect on copper deposition when MPS was present and PEG was absent in the electrolyte, even when the rotation speed of the WE was 2500 rpm. Under this condition, the positive-going curve of PEG + Cl\(^-\) + JGB significantly deviated from that of PEG + Cl\(^-\), which is attributed to the rapid replenishment of chloride ion and JGB (see Discussion). However, if the JGB concentration was 1 ppm, the positive-going curve of the composite suppressor almost entirely superposed the polarization curve of PEG + Cl\(^-\), indicating that high JGB concentration and strong forced convection were significant factors in maintaining the synergistic inhibition effect.
action. When PEG was present in the electrolyte, a competitive electrochemical behavior among these additives was characterized by the CLSV, as shown in Fig. 10. In particular, when the rotation speed of the WE was increased to 2500 rpm, a significant hysteresis loop was obtained, indicating that the composite suppressor was able to compete with the accelerator due to the assistance of forced convection.

The aforementioned results indicate that the surface additive composition working on the copper deposit was not absolutely determined by the additive composition of the bulk solution but was dependent on the location of the copper deposit, the strength of the forced convection, and the overpotential of the cathode. Moreover, the dominance of an additive in the competitive adsorption was not certainly maintained throughout the electroplating process. It also depended on certain factors, including chemical and physical events. The following discussion further reveals the detailed mechanism of the synergy.

Discussion

Adsorption of PEG, JGB, and Cl⁻.— It was reported that the adsorption of chloride ion on the copper surface is potential-dependent, especially at a concentration lower than 20 ppm. However, when the chloride ion concentration is higher than 20 ppm, the potential-dependent adsorption of chloride ion on the copper surface is not significant. This finding was attributed to the formation of CuCl precipitate. The adsorption of chloride ion on the copper surface can immediately result in the formation of Cu⁺-Cl⁻, which was demonstrated to be the adsorbing site for PEG adsorption on the copper surface. Consequently, it also led to a potential-dependent adsorption of PEG.

Many articles have reported that PEG-Cu⁺-Cl⁻ is an effective barrier for copper deposition. Therefore, the coverage of chloride ion on the copper surface is a critical factor for the inhibition effect of PEG-Cu⁺-Cl⁻ on copper deposition. Alternatively, the mass transfer of chloride ion toward the cathode dominates the inhibition performance of PEG-Cu⁺-Cl⁻ when the chloride ion concentration is constant.

Regarding the transport of chloride ion to the cathode during electroplating, three physical terms, diffusion, migration, and convection, are generally considered as follows:

$$J_{Cl^-} = -D_{Cl^-} \nabla C_{Cl^-} - \frac{C_{Cl^-}}{RT} D_{Cl^-} C_{Cl^-} \nabla \Phi + C_{Cl^-} \frac{F}{n f}$$

If the consumption of chloride ion caused by inclusion in copper deposit is negligible, Eq. 1 can be reduced to one term, namely, convection. The migration caused by an electric field gives rise to an opposite effect on the transport of chloride ion because of its negative charge. This situation becomes more significant in the microvia as the electric field effect is almost three-dimensional. Hence, chloride ions do not easily migrate to the bottom of the microvia if forced convection is weak during electroplating. Once the chloride ion concentration becomes low, the potential-dependent adsorption of chloride ion on the copper surface will be the adsorbing site for PEG adsorption on the copper surface. Consequently, it also led to a potential-dependent adsorption of PEG. The mass transfer of chloride ion toward the cathode dominates the inhibition performance of PEG-Cu⁺-Cl⁻ when the chloride ion concentration is constant.

To confirm the convection-dependent adsorption of PEG-Cu⁺-Cl⁻ at a low chloride ion concentration, steady-state polarization curves were carried out using different WE rotation speeds. As shown in Fig. 11, when the potential of the WE was lower than −0.6 V (i.e., more positive) and the chloride ion concentration was 10 ppm, the inhibition effect on copper deposition was reduced with increasing the rotation speed. When the potential of the WE was
higher than −0.6 V (i.e., more negative), a significant rise in current was observed and the inhibition effect of PEG + Cl\textsuperscript{−} was enhanced with increasing the rotation speed. These behaviors are attributable to the potential-dependent adsorption of chloride ion\textsuperscript{14,22,23} With more positive potential and lower chloride ion concentration, Cu\textsuperscript{2+}\textsuperscript{−}Cl\textsuperscript{−} is the predominant species on the copper surface. Therefore, PEG can be strongly adsorbed on the copper surface to block copper deposition. At the same time, Cu\textsuperscript{2+} transport by the forced convection is the limiting step for the generation of cathodic current. Hence, the faster the rotation speed, the larger the cathodic current.

When the potential is higher than −0.6 V, chloride ions desorb physically from the copper surface, leading to a marked rise in current as shown in the case of 10 ppm Cl\textsuperscript{−}. At the same time, the transport of chloride ion toward the cathode is the main factor that dominates the current of copper deposition. Consequently, the faster the rotation speed, the smaller the cathodic current. Namely, forced convection can effectively assist the transport of chloride ion toward the cathode as mentioned previously. Similar results were also observed by Kondo et al.\textsuperscript{15}

However, when the chloride ion concentration was higher than 20 ppm, CuCl precipitates were the predominant species on the copper surface\textsuperscript{22,23,28,29} and resulted in a disappearance of potential-dependent adsorption of chloride ion on the copper surface\textsuperscript{22,23} According to previous works\textsuperscript{21,28,29}, cupric ions are reduced by two different paths at high chloride ion concentration. One is a direct discharge as expressed by Reaction 2; the other is a parallel path through copper chloride precipitate as expressed by Reaction 3

\[
\text{Cu}^{2+} + e^{-} \rightarrow \text{Cu}^{0} \quad [2]
\]

\[
\text{CuCl} + e^{-} \rightarrow \text{Cu} + \text{Cl}^{-} \quad E_{\text{SSE}}^{0} = -0.513 \text{ V} \quad [3]
\]

Related investigations have demonstrated that the formation rate of CuCl precipitate on the copper surface is chloride ion mass-transfer controlled\textsuperscript{30,31}. Hence, strong forced convection can enhance the rate of CuCl formation, subsequently leading to a slight increase in the current of copper deposition due to Reaction 3, as shown in Fig. 11. The electrochemical reduction of CuCl precipitates immediately releases chloride ions on the cathodic surface to form a PEG-Cu\textsuperscript{2+}Cl\textsuperscript{−} complex film.\textsuperscript{11} Therefore, when the potential of WE shifted to −0.65 V, the inhibition effect of 200 ppm PEG + 90 ppm Cl\textsuperscript{−} is markedly stronger than that of 200 ppm PEG + 10 ppm Cl\textsuperscript{−}; additionally, the potential- and convection-dependent inhibition effect of PEG-CI\textsuperscript{−} on copper deposition is not obvious in the case with 90 ppm Cl\textsuperscript{−} due to the easy formation of CuCl precipitate.

For JGB adsorption on the copper surface, the increase in chloride ion concentration also enhanced the inhibition effect of JGB on the copper deposition and led to a marked hysteresis loop in CLSV, as shown in Fig. 12. Comparing Fig. 7 with Fig. 12, either increasing the chloride ion concentration or speeding up the convection led to an enhanced inhibition effect of JGB on copper deposition. These results are attributed to the potential-dependent adsorption of chloride ion and to the mass-transfer limitation of JGB\textsuperscript{8,15,17}.

Composite suppressor vs. convection-dependent adsorption.— In the presence of Cl\textsuperscript{−}, the synergistic inhibition effect of PEG with JGB on copper electrodeposition was confirmed to be potential- and convection-dependent, in which the inhibition degree is much greater than that of PEG + Cl\textsuperscript{−} or JGB + Cl\textsuperscript{−}. This adsorptive and inhibitive behavior of PEG + JGB + Cl\textsuperscript{−} is related with the surface coverage of chloride ion on the copper surface. If PEG was not present in the electrolyte, as shown in Fig. 7 and 12, JGB could not exhibit a strong inhibition effect on copper deposition. If PEG was
present in the electrolyte and the forced convection was strong, the synergistic inhibition effect of PEG with JGB occurred, even at high cathodic potential, as shown in Fig. 8. These results suggest that the synergistic inhibition effect caused by the composite suppressor, PEG-Cl−-JGB, is convection-dependent and related to the transport of Cl− by forced convection.

When both PEG and JGB are coadsorbed on the copper surface, the composite suppressor becomes more compact to block the transport of Cu2+ to the cathodic surface. Similar to the transport of Cu2+, the transport of chloride ion to the cathode also becomes difficult due to the blocking effect of the composite suppressor. Consequently, chloride ion must pass through the composite suppressor by means of the diffusion mode. Hence, forced convection becomes considerably important because the inhibition effect of the composite suppressor must be maintained by a continuous supply of chloride ion through the composite suppressor to the cathodic surface.

Alternatively, if the rotation speed of WE is constant, it is reasonable to expect that the inhibition effect of the composite suppressor is sensitive to the chloride ion concentration. A coincident outcome is demonstrated by LSV measurements shown in Fig. 13. The degree of inhibition of the composite suppressor is obviously enhanced with increasing the chloride ion concentration. Thus, the convection-dependent adsorption of the composite suppressor can be explained by correlating the adsorptive characteristics of chloride ion with the transport of chloride ion.

Competitive adsorption vs. forced convection.—When MPS was added to the electrolyte and JGB was absent, a competitive adsorption between the accelerator and the suppressor occurred.11 The finally predominant species on the copper surface were determined by the strength of forced convection.12 A similar outcome still occurred when JGB was present in the electrolyte, as shown in Fig. 14. When the rotation speed of WE was slow and the JGB concentration was low, the predominant species adsorbed on the copper surface was accelerator. This situation resembles that at the bottom of the microvia. The composite suppressor dominated the copper deposition at fast rotation speed and at high JGB concentration, of which the situation resembles the condition on the board surface during electroplating. Consequently, bottom-up deposition occurred because there was a potential gap between the via bottom and the board surface.

However, not only the forced convection but also the chloride ion concentration governed the competitive adsorption. This inference was confirmed by GMs, as shown in Fig. 15. It is evident that at any rotation speed, the cathodic potential during the electroplating was dominated by the chloride ion concentration. As the chloride ion concentration increased, the inhibition effect strengthened and the replacement time from depolarization to polarization was reduced. These results support two points: the composite suppressor cannot compete with the accelerator at a low chloride ion concentration and the accelerator does not easily compete with the composite suppressor at strong forced convection. Figure 15 also demonstrates that almost all chloride ions interacted mainly with MPS, resulting in an acceleration effect.11,12 When the chloride ion concentration was low. There was an obvious potential gap between curve...
two reaction paths may proceed as follows

\[ R - S^- + Cu^+ + Cl^- + e^- \rightarrow Cu + R - S^- + Cl^- \]  

[5]

Reaction 4 leads to a depolarization of the cathode, whereas Reaction 5 leads to a polarization of the cathode in the GM. Furthermore, the reduction potential of Reaction 3 is similar to that of Reaction 4, which occurs exactly at \(-0.513 \text{ V vs. SSE}\). Hence, the potential oscillation is associated with the competition between Reactions 4 and 5. After the potential oscillation, Reaction 5 was dominant and resulted in the significant potential drop, as shown in Fig. 15.

At the bottom of the microvia, the chloride ion concentration was relatively lower than at board surface due to the transport consideration, and the forced convection was relatively weaker compared with that at the board surface. Ideally, bottom-up fill occurs if the concentration ratio of the suppressor to the accelerator is appropriate. However, once the concentration ratio of the suppressor to the accelerator deviates from a specific balance value, the asymmetric bottom-up deposition occurs, as shown in Fig. 2 and 3, because the impact of the fluid acting at area A is stronger than that at area B, as shown in Fig. 4. The different morphologies of the copper deposits caused by the same formula shown in Fig. 6 can also be explained by the convection-dependent adsorption behavior of these additives, where the fine-grained copper deposit at the top area of the filled microvia is caused by the accelerator-dominant composition and the coarse-grained copper deposit at the other places is caused by the suppressor-dominant composition.

Conclusions

The filling performance of a plating formula for microvia metalization can be conspicuously improved by the addition of a leveler. The enhancement in filling performance results from a synergistic inhibition effect caused by a composite suppressor composed of PEG, chloride ion and JGB. The synergistic inhibition effect of the composite suppressor on copper deposition is strongly dependent on the forced convection and on the chloride ion concentration. This dependence is attributed to the potential-dependent adsorption of chloride ion on the copper surface and to the mass-transfer limitation of JGB.

Strong forced convection and high chloride ion concentration are beneficial to the action of the composite suppressor on the copper surface, whereas weak forced convection and low chloride ion concentration are beneficial to the action of the accelerator on the copper surface. The final dominance of the competitive adsorption between the composite suppressor and the accelerator is determined by both the forced convection and the chloride ion concentration. Hence, a consideration of fluid dynamics and a precise analysis of chloride ion during electroplating are crucial factors for achieving an excellent filling performance.

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List of Symbols

\( C_{Cl^-} \) concentration of chloride ion, mol cm\(^{-3}\)
\( D_{Cl^-} \) diffusion coefficient of chloride ion, cm\(^2\) s\(^{-1}\)
\( F \) Faraday constant, 96,487 C
\( J_{Cl^-} \) flux of chloride ion, mol cm\(^{-2}\) s\(^{-1}\)
\( R \) ideal gas constant, 8.314 J mol\(^{-1}\) K\(^{-1}\)
\( T \) temperature, K
\( v \) velocity of bulk solution flow, cm s\(^{-1}\)

\( \mathrm{Cl}^- \) charge of chloride ion

Greek

\( \Phi \) electrostatic potential, V

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