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The Synergistic Effect between a Triblock Copolymer and Chloride Ions in Cu Electrodeposition into Microvias

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Interactions between a triblock copolymer, commercially named Pluronic L64, and chloride ions (Cl^-) was found efficient for Cu electrodeposition in microvia filling process. Cyclic voltammetry (CV) curves clearly showed the synergistic effect between L64 and Cl^- to inhibit copper electrodeposition. CV stripping measurements further suggested that the possible synergistic effect was dependent on the concentrations of L64 and Cl^-. With a fixed L64 concentration ($\geq$ 7.5 ppm), there was a proper Cl^- concentration to achieve the maximum synergistic effect. Haring cell experiments confirmed that the results obtained from CV stripping tests can be used for guiding microvia filling experiments.
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In a microvia filling process, superfilling can be achieved by using an acidic copper sulfate electroplating bath containing at least a suppressor and an accelerator.[1–3] Generally, the accelerator is 3-mercapto-1-propanesulfonate (MPS) or bis (3-sulfopropyl) disulfide (SPS), which has a synergistic effect with Cl^- to accelerate the copper deposition in the bottom of the microvia.[4–6] The suppressor is usually polyethylene glycol (PEG)[7–10] or block copolymers, such as the triblock copolymers of L64.[11–13] It has been demonstrated that PEG can react with Cu^+ and Cl^- to form a complex film adsorbing on copper surface to inhibit copper deposition outside the microvia.[14]

To the best of our knowledge, while there are many investigations about PEG in microvia filling process, only few literatures refer to the block copolymers.[15] Compared with PEG, block copolymer composed of polyethylene oxide (PEO) and polypropylene oxide (PPO) has many controllable factors, such as the ratio of EO to PO, PEO-PPO diblocks and PEO-PPO-PEO triblocks, etc.[11,12] With a molecular formula of $EO_{13}PO_{30}EO_{13}$, Pluronic L64 can form micelles in aqueous solutions with a hydrophobic core composed of PPO blocks and an outer shell consisting of hydrated PEO.[13] These unique properties may make L64 exhibiting some different properties in the microvia filling process.

In this work, the synergistic effect between L64 and Cl^- on inhibiting copper deposition is investigated by electrochemical measurements. The synergistic effect as function of L64 and Cl^- concentrations is discussed in details, which is in agreement with the Haring cell experiments.

Experimental

A Haring cell with working volume of 1500 mL and a phosphorus-containing (0.03-0.065%) copper plate were used as the electroplating vessel and anode, respectively. Printed circuit boards (4 × 9 cm^2) with many blind holes formed by CO_2 laser ablation were used as test samples for filling plating. The diameter and depth of the holes were 150 μm and 75 μm respectively. The hole wall was metallized by electroless copper plating for 2–3 μm copper film.

Before electroplating, the sample was activated in 10 wt% H_2SO_4 solution for 1 min and then predipped in the plating bath for 5 min to completely wet the via holes. At the beginning of the electroplating, current density was controlled at 1 A/dm^2 for 30 min and then switched to be 2 A/dm^2 for 90 min. During electroplating, agitation by continuous air bubble flow (forced convection) was sustained to ensure an efficient mass transfer.

The standard electrolyte for via filling plating was composed of 220 g/L $CuSO_4 \cdot 5H_2O$, 55 g/L H_2SO_4, 3 ppm SPS, 4 ppm Janus Green B (JGB), as well as Cl^- (added as HCl) and L64. Pluronic L64 (triblock copolymer: $EO_{13}PO_{30}EO_{13}$) was obtained from BASF Corp. The copolymer has a nominal molecular weight of 2900 and approximately 40 wt% EO. The temperature of the plating solution was maintained at 25 °C.

The filling capacity of the microvia was examined by optical microscopy (DFC290, Leica) for cross-sectional views. The synergistic effect between Cl^- and L64 was analyzed by CV stripping (797 VA Computrace, Metrohm). A platinum rotating disk electrode with a diameter of 3 mm and a platinum bar were used as the working electrode and the counter electrode, respectively. The reference electrode was Ag/AgCl (3 mol/L KCl) electrode, which was placed in a small teflon tube that contained 1 mol/L KNO_3 solution. The end side of the teflon tube was sealed with a porous polymer material. The base electrolyte (30 mL) for CV testing was composed of 220 g/L $CuSO_4 \cdot 5H_2O$ and 55 g/L H_2SO_4. In CV measurements, different amounts of L64 and Cl^- were added continuously. The rotation speed of the working electrode was fixed at 2600 rpm. The CV measurements were carried out by a negative-going sweep from 1.625 V to −0.250 V, followed by a positive-going sweep from −0.250 V to 1.625 V, with a scan rate of 0.1 V/s.

Results and Discussion

After the addition of Cl^- into the base electrolyte, the area of copper stripping peak increases obviously and the initial potential of copper deposition shifts toward more positive as shown in Fig. 1a. It indicates that Cl^- is a good depolarizer for copper electrodeposition. The addition of L64 can result in a decrease of the copper stripping peak area as well as a shift of initial potential of copper deposition toward more negative. These phenomena suggest that L64 can suppress copper deposition.

Interestingly, the area of copper stripping peak sharply decreases when Cl^- and L64 are added into the base electrolyte together. As shown in Fig. 1b, the current density on the negative-going sweep is larger than that on the positive-going sweep between line a and line b. This is similar to the performance of the curve obtained in base electrolyte with Cl^-. While the current density on the negative-going sweep is lower than that on the positive-going sweep between line b and line c, which is in agreement with the curve obtained in base electrolyte with L64. Based on the above results, it can be concluded that there is a synergistic effect between L64 and Cl^- in suppressing copper deposition. In addition, L64 and Cl^- should present different adsorption-desorption behavior on the working electrode, such as the adsorption-desorption potential or rate, which simultaneously influence the tendency of the CV curve obtained in base electrolyte with L64 and Cl^-.

To gain more insight into the synergistic effect between Cl^- and L64, a series of CV measurements were performed as shown in Fig. 1c and 1d. It can be seen from Fig. 1c that each plot has a minimum except for the cases in the electrolyte with 0 ppm and 5 ppm L64. It should be pointed out that the synergistic effect

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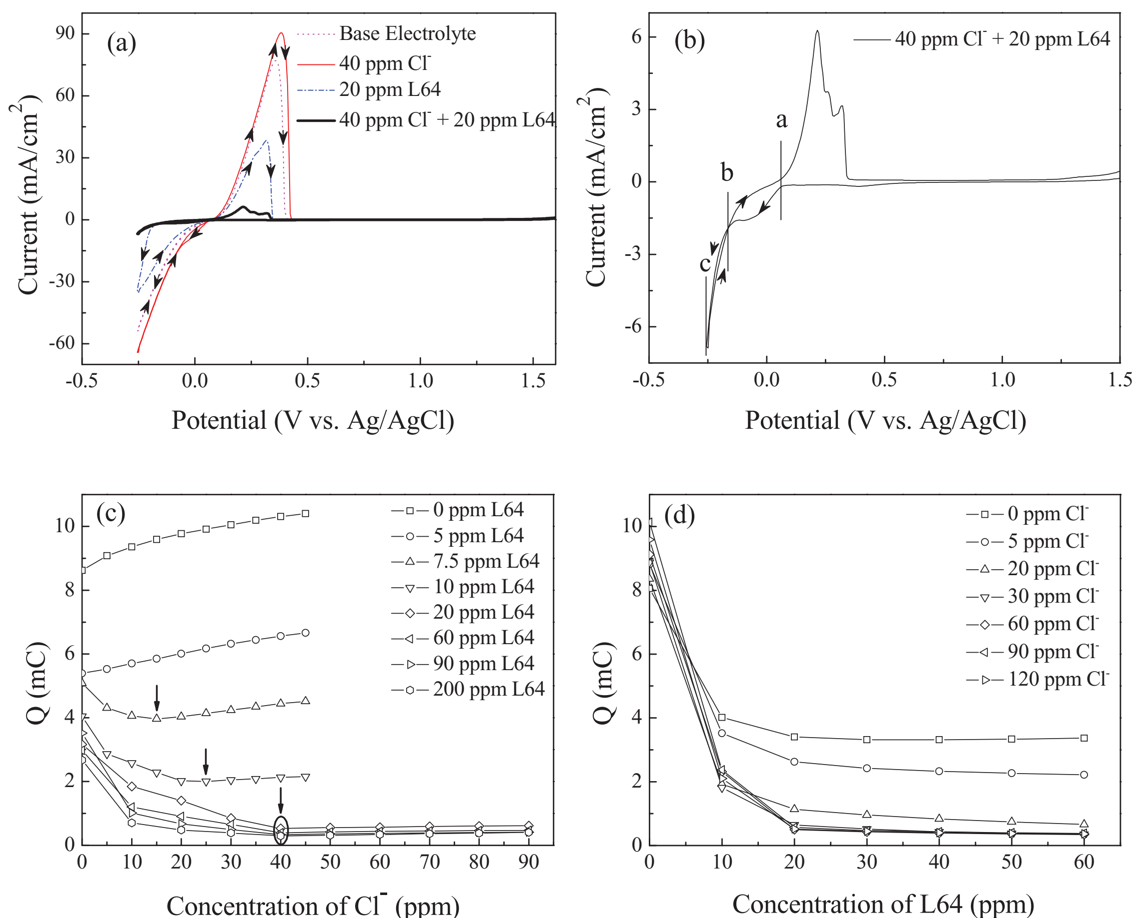

Figure 1. (a) CV curves obtained in base electrolyte with and without additives; (b) magnified curve obtained in base electrolyte with 40 ppm Cl^- and 20 ppm L64; (c) and (d) CV stripping measurements of Q value as a function of the concentrations of Cl^- and L64. Here Q is the integral value of the copper stripping peak. The base electrolyte is composed of 220 g/L $CuSO_4 \cdot 5H_2O$ and 55 g/L H_2SO_4.

between Cl^- and L64 is the most manifested at the minimum, that is, the suppression of copper deposition by L64 and Cl^- is strongest. Moreover, it is noted that the minimums maintain at 40 ppm of Cl^- and no longer increase when the concentration of L64 is higher than 20 ppm, which suggests that 40 ppm is quite enough for Cl^- to interact with L64 molecules to adsorb on the working electrode.

As shown in Fig. 1d, no matter how much chloride ions are premixed with the base electrolyte, the Q values show very little changes when the addition amount of L64 is higher than 20 ppm. It suggests that with proper concentration of Cl^- (such as 40 ppm), 20 ppm L64 is enough to form an intact barrier layer on the cathode surface to suppress copper deposition. More L64 molecules lead to a thicker barrier layer. This can explain the little decrease of Q values with the increasing concentration of L64 ($\geq$ 20 ppm). On the contrary, if the concentration of L64 is lower than 20 ppm, the adsorbed L64 micelles cannot form a continuous barrier film, which may result in more copper deposition on the surface where is not covered by L64 micelles.

To prove the above views, Haring cell experiments are carried out in base electrolyte only with L64 and Cl^-. As shown in Fig. 2(a1)–2(a3), until the concentration of L64 increases to 20 ppm, the nodules on the board surface completely disappear. The lower L64 concentration, the more nodules on the board surface.

The optical microscopy images of other two groups of Haring cell experiments performed in the standard electrolyte with different concentrations of L64 and Cl^- are shown in Fig. 2(b1)–2(b3) and Fig. 2(c1)–2(c3) respectively. It can be observed from Fig. 2(b1) that

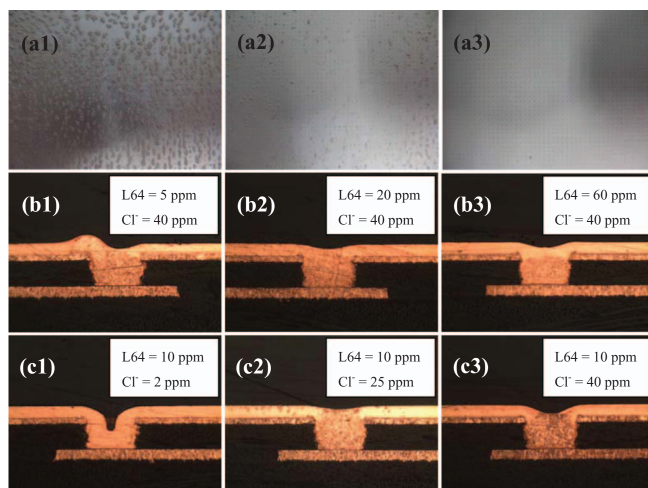

Figure 2. Top views (taken by a camera) of the samples obtained in base electrolyte only with Cl^- and L64: (a1) 5 ppm L64 and 40 ppm Cl^-; (a2) 10 ppm L64 and 40 ppm Cl^-; (a3) 20 ppm L64 and 40 ppm Cl^-. (b1)-(b3) and (c1)-(c3) cross-sectional optical microscopy pictures of microvias after filling plating. Standard electrolyte for via filling plating is composed of 220 g/L $CuSO_4 \cdot 5H_2O$, 55 g/L H_2SO_4, 3 ppm SPS and 4 ppm JGB. The kind and addition amount of additives are illustrated in each picture. All OM magnifications are 200×.

there is a nodule on the board surface. Actually, there are many nodules on the board surface similar to that shown in Fig. 2(a2), which can be attributed to the discontinuous barrier film. When the concentration of L64 increases to 20 ppm, a continuous barrier film can be formed on the board surface. As shown in Fig. 2(b2), the board surface after electroplating is smooth. If the concentration of L64 continues to increase, the appearance and thickness of copper film deposited on the board surface almost has no changes as shown in Fig. 2(b3). It can be obtained from Fig. 2(c1)–2(c3) that when L64 concentration is fixed at 10 ppm and Cl^- concentration increased from 2 ppm to 40 ppm, the filling performances first get better and then get worse. When the concentrations of L64 and Cl^- are 10 ppm and 25 ppm respectively, just the minimum in Fig. 1c, the filling performance is the best.

All the above results obtained from Haring cell experiments are consistent with CV results. However, there are also some differences between the two measurements. As shown in Fig. 2(c3), with 10 ppm L64 and 40 ppm Cl^- in the plating bath, the thickness of deposited copper film on the board surface is the same to that of the sample shown in Fig. 2(b2). Moreover, it also has a smooth board surface (not shown here) similar to that shown in Fig. 2(a3). These results suggest that a continuous barrier film can also be formed on the board surface with a lower L64 concentration of 10 ppm, which can be explained by the adsorption of JGB molecules on the vacancies left by insufficient L64 micelles to form an intact barrier film. Because JGB molecules are positively charged and small enough to adsorb on the cathode surface, on which L64 micelles are not adsorbed.

Conclusions

CV curves clearly showed the synergistic effect between L64 and Cl^- on inhibiting copper deposition. A series of CV tests further explored the influences of the concentrations of L64 and Cl^- on the synergistic effect, which indicated that with a fixed concentration of L64 ($\geq$ 7.5 ppm), there existed an optimal concentration of Cl^- to achieve the maximum synergistic effect. Haring cell experiments confirmed that the conclusions of CV measurement can be used for guiding microvia filling experiments. In addition, the combinations of 10 ppm L64 with 25 ppm Cl^- and 20 ppm L64 with 40 ppm Cl^- were the most excellent in these microvia filling formulas.

Acknowledgments

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