

Effects of Organic Additives on Residual Stress and Surface Roughness of Electroplated Copper for Flexible PCB

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For the application of flexible printed circuit board (FPCB), electroplated copper is required to have low surface roughness and residual stress. In the paper, the effects of surface roughness and residual stress of electroplated copper as thick as 8 μ m were studied on organic additives such as inhibitor, leveler and accelerator. Polyimide film coated with sputtered copper was used as a substrate. Surface roughness and surface morphology were measured by 3D-laser surface analysis and FESEM, respectively. Residual stress was calculated by Stoney's equation after measuring radius curvature of specimen. The addition of additives except high concentration of accelerator in the electrolyte decreased surface roughness of electroplated copper film. Such a tendency was explained by the function of additives among which the inhibitor and the leveler inhibit electroplating on a whole surface and protrusions, respectively. The accelerator plays a role in accelerating the electroplating in valley parts. The inhibitors and the leveler increased residual stress, whereas the accelerator decreased it. It was thought to be related with entrapped additives on electroplated copper film rather than the preferred orientation of electroplated copper film. The reason why additives lead to residual stress remains for the future work.

Keywords: flexible printed circuit board, electroplating, copper, additive, residual stress, surface roughness

1. Introduction

In general, FPCB (Flexible Printed circuit Board) consists of a polyimide film as an insulator with low dielectric constant and an electroplated copper film as an excellent conductor. It has been applied to complicated electronic devices and repetitive moving parts such as materials of Liquid Crystal Display (LCD), Tape Automated Bonding (TAB) and Chip on Flexible Printed Circuit (COF), and so on. The residual stress and the surface roughness of the electroplated copper film are required to be low and thereby to have high reliability. Therefore, organic additives usually classified as inhibitor, leveler and accelerator certainly need in order to satisfy the requirements.

As inhibitors with 100~100,000 molecular weight, polymers including oxygen suppress charge transfer on the electrode surface during plating.^{1,2)} There are polyethylene glycol (PEG), polyethylene oxide (PEO), polypropylene glycol (PPG), gelatin, and so on. The inhibiting action is explained by adsorption of inhibitor-Cl complex with chloride ion^{1,3)-6)} behaving as uniform barrier to suppress

charge transfer.^{1,7)} As levelers, organic compounds including nitrogen such as benzotriazole (BTA), janus green B (JGB), and so on also suppress charge transfer on the electrode surface during plating. However, levelers effecting transport in electrolyte are preferentially adsorbed on the sites such as protrusions and corners to prevent formation of protrusion.^{5),8)-10)} As accelerators, the following organic compounds including sulfur promote charge transfer on the electrode surface: 3-mercapto-1-propane sulfonic acid (MPSA), Bis-(3-sodiumsulfopropyl) disulfide (SPS), 3-N,N-dimethylaminodithiocarbamoyl-1-propanesulphonic acid (DPS), etc. According to curvature-enhanced accelerator coverage (CEAC) model,¹¹⁾ surface roughness of copper film decreases due to accumulation of accelerator in valley parts. In addition, accelerators are known to retard surface diffusion and to result in more bright and smooth plated surface.^{12),13)} Min Tan et al.¹¹⁾ showed that smooth copper film was obtained from the addition of SPS as low as 1 ppm. Vas'ko et al.¹⁴⁾ and Lee et al.⁸⁾ reported that r.m.s roughness value decreased from 250 nm to 10 nm with DPS as an accelerator and from 61 nm to 7.9 nm with JGB as a leveler, respectively.

On the other hand, the effects of additives on residual

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stress have been much less understood than those on surface roughness. The residual stress of electroplated film depending on applied current, solution composition and other plating conditions is known to be caused during the coalescence of grains or parts of them growing laterally from different nucleation centers.¹⁵⁾ However, the occurrence of the residual stress has been explained with over-voltage,¹⁶⁾ surface energy and strain energy¹⁷⁾⁻¹⁹⁾ and the co-depositions of impurities,²⁰⁾⁻²³⁾ which depended on the kinds of organic additives and their concentrations. Therefore, the aims of this work are to examine the effects of organic additives on residual stress as well as on surface roughness of electroplated copper film and to find the roles of the organic additives.

2. Experimental

A polyimide film (Dupont) coated with sputtered copper as thick as 2000 Å was used as a cathode electrode. A phosphorized copper plate (containing 0.05% phosphorus) was used as an anode electrode. The basic electrolyte was composed of 72 g/L CuSO₄·5H₂O, 180 g/L H₂SO₄ and 30 ppm Cl⁻. The electrolyte temperature was kept constant at 25±1 °C. Electroplating was carried out in a stagnant solution under the constant current of 13 mA/cm² until the copper film approached to 8 μm thick.

The residual stress of the electroplated copper film was calculated according to equation (1) and measurements of curvature radii before and after plating.²⁴⁾ For these measurements, the electroplated copper films of 5 cm×0.5 cm size were used.

$$\sigma = \frac{E_s t_s^2}{6(1-\nu_s)t_f} \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \quad (1)$$

where σ_f is the stress of the copper film, E_s is the elastic modulus of the polyimide film (=5,379MPa), t_s is thickness of the polyimide film (=38μm), ν_s is the poisson's ratio of the polyimide film (=0.32), t_f is the thickness of the copper film and r_1 and r_2 is the curvature radius of the film before and after plating, respectively. The curvature radius was calculated according to equation (2) and Fig. 1.²⁵⁾

$$r = \frac{L^2 + \delta^2}{2\delta} \quad (2)$$

Average surface roughness (R_a , R_z) of electroplated copper film was measured by 3D laser surface analysis in 256 x 192 μm areas. In addition, field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD)

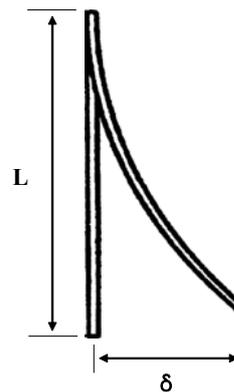


Fig. 1. Measurements of radius of copper plated film.

was employed to examine the surface morphologies of the electroplated copper films and to determine the texture coefficient of the plated copper films, respectively.

The texture coefficient, TC of the (hkl) plane is defined by equation (3).

$$TC(hkl) = n \frac{I(hkl)/I_o(hkl)}{\sum I(hkl)/I_o(hkl)} \quad (3)$$

where $I(hkl)$ and $I_o(hkl)$ are the integrated intensities of (hkl) reflections measured for the copper plated film and a standard copper powder sample, respectively and n is the total number of reflection planes.

3. Results and discussion

3.1 Surface roughness with additives

Fig. 2 and Fig. 3 show that the inhibitor and the leveler decreased surface roughness. Especially, the leveler more effectively decreased surface roughness (R_a) from about 640 nm to 40 nm. The effectiveness of the leveler in decreasing surface roughness is due to the difference in inhibiting electroplating; in other words, the leveler is preferentially adsorbed on the sites accessible to suppress the electroplating,^{5),8)-10)} while the inhibitor complexed with chloride ion is adsorbed on the whole surface^{1),7)} though the complex is preferentially adsorbed on the defects of step, kink, hole and edge in an atomic scale as well as inhibit the lateral growth of macrosteps.⁹⁾ The difference in role between the inhibitor and the leveler is confirmed with comparison between the photographs of Fig. 5 (a) and Fig. (b), showing that protrusions on the copper film were suppressed by the leveler.

Like the other additives, the accelerator allowed surface roughness to be low at the range of the concentration of the leveler between 0 and 5 ppm, after a critical concentration of the accelerator, made surface roughness high as

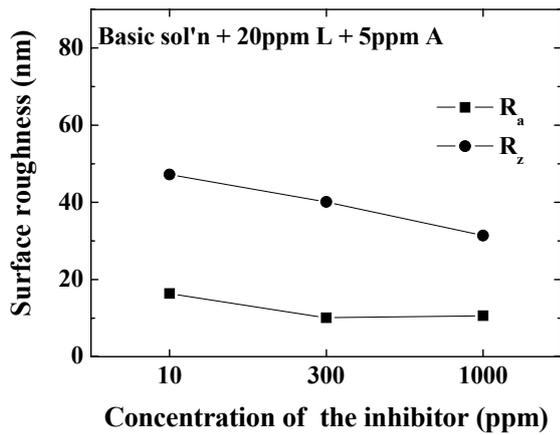


Fig. 2. Surface roughness with the concentration of the inhibitor (I: inhibitor, L: leveler, A: accelerator).

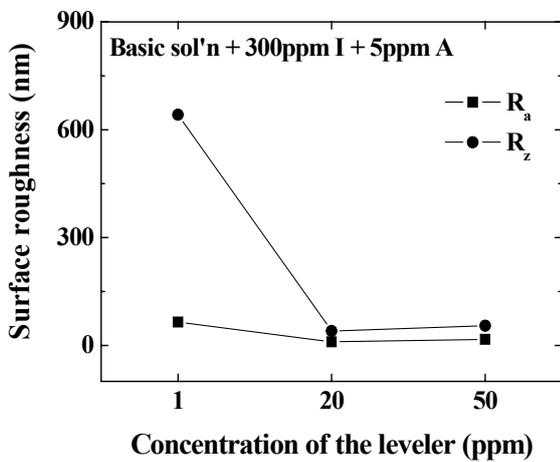


Fig. 3. Surface roughness with the concentration of the leveler (I: inhibitor, L: leveler, A: accelerator).

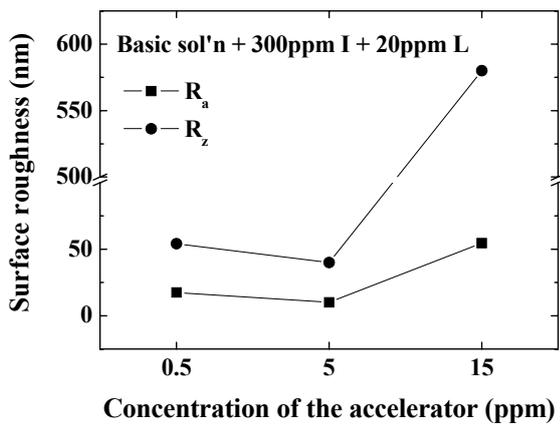
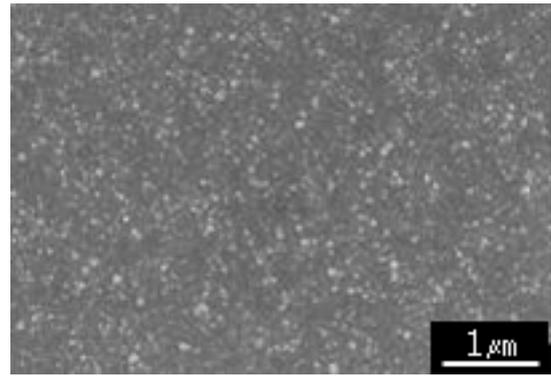
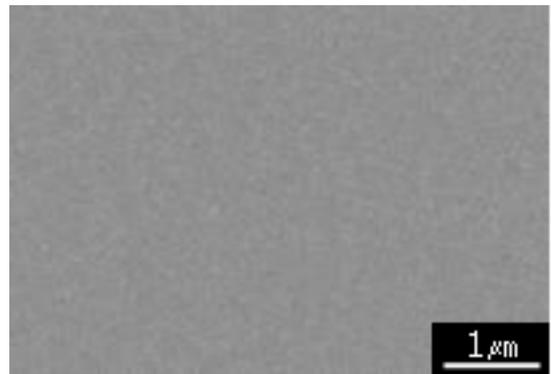


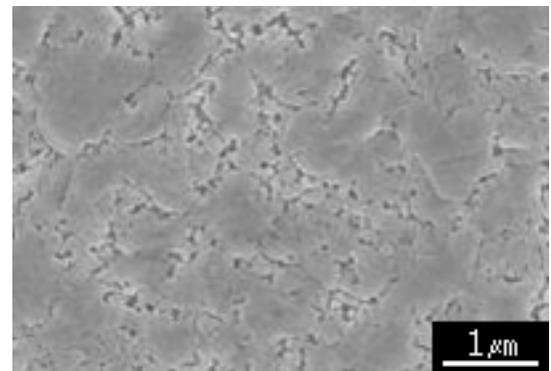
Fig. 4. Surface roughness with the concentration of the accelerator (I: inhibitor, L: leveler, A: accelerator).



(a)



(b)



(c)

Fig. 5. FESEM images showing surface roughness with additives and their concentrations: (a) 300ppm I + 5ppm A; (b) 300ppm I + 20ppm L + 5ppm A; (c) 300ppm I + 20ppm L + 15ppm A (I: inhibitor, L: leveler, A: accelerator).

shown in Fig. 4. This behavior could be explained by the curvature enhanced accelerator coverage (CEAC) model,¹¹⁾ where, as the valley is filled during electroplating, the decrease of surface area inside the valleys increases the surface concentration of the accelerator to increase the plating rate inside the valleys. In the other words, valleys have higher plating rate than flat surfaces and thereby make

surface smoother. However, too high concentration of the accelerator did not provide the difference in the concentration of the accelerator between inside valley and outside valley to lead to make film surface rough in Fig. 5 (c).

3.2 Residual stress with additives

Residual stress was increased with inhibitor and leveler in Fig. 6 and Fig. 7. However, the accelerator provided the opposite trend in residual stress in Fig. 8. In addition, Table 1 shows that the accelerator caused preferred plane to be changed from (220) to (200) as well as decreased the residual stress. Based on the results, the organic additive can be thought to determine the preferred plane and thereby to decide the residual stress. On the other words, the formation of preferred (111) plane having higher elastic strain energy lead to higher residual stress and the formation of preferred (100) plane having lower elastic strain energy lead to lower residual stress.^{18),19)} However, the appearance of residual compressive stress with the addition of 5ppm of the accelerator in Fig. 8 and the increase of texture coefficient of (111) plane with the accelerator can not be explained by the above proposal.

Hence, it is necessary that the effect of organic additives on residual stress would be explained with the other. Here, the effect of organic additives on residual stress would be thought to be explained with entrapped impurity model,^{23),26)} which organic additives are co-deposited during plating to cause residual stress. Furthermore, both of residual tensile stress and residual compressive stress are able to be explained with the types of sites where organic additives are located, substitutional site and interstitial site: organic additives located on substitutional sites during plating lead to residual tensile stress, whereas other organic additives located on interstitial sites lead to residual compressive stress. According to the entrapped impurity model, the inhibitor and the leveler are thought to be entrapped into substitutional sites during plating and the accelerator is thought to be entrapped into interstitial sites though the data are too lacking in supporting the above model. That fact that the inhibitor was observed in the plated copper film^{14),19)} is believed to support the entrapped impurity model in some extent. The analyses showing that the additives are co-deposited in the plated film and the experiments providing that residual stress is independent of texture will be required in order to approve the above model, which are left for the future works.

4. Conclusions

In this paper, surface roughness and residual stress of the electroplated copper film were investigated and the

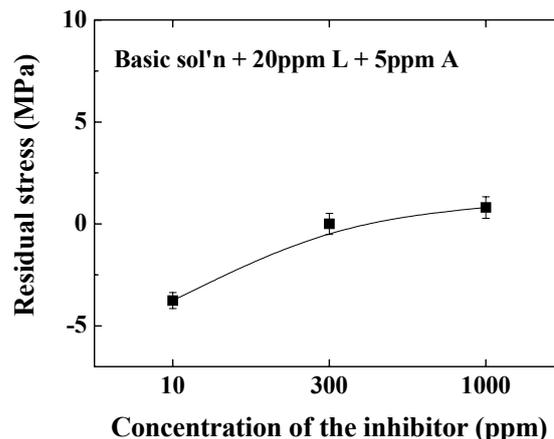


Fig. 6. Residual stress with the concentration of the inhibitor (I: inhibitor, L: leveler, A: accelerator).

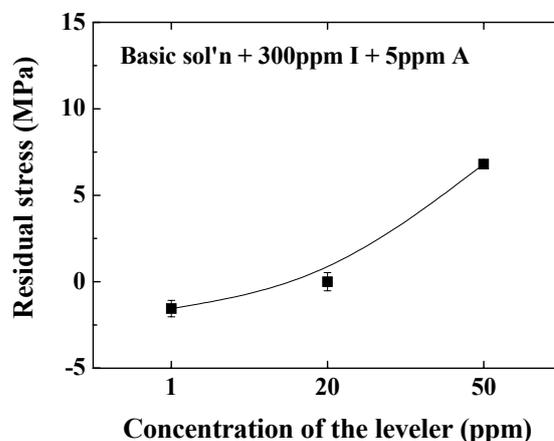


Fig. 7. Residual stress with the concentration of the leveler (I: inhibitor, L: leveler, A: accelerator).

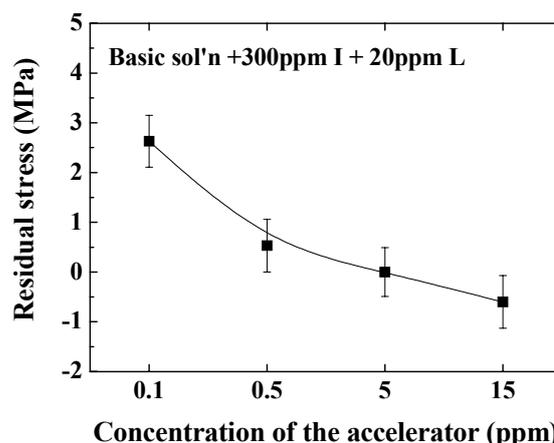


Fig. 8. Residual stress with the concentration of the accelerator (I: inhibitor, L: leveler, A: accelerator).

Table 1. Relation between residual stress and preferred plane formed during plating (I: inhibitor, L: leveler, A: accelerator).

Electrolyte	Texture coefficient			Residual stress (MPa)	Preferred plane
	(111)	(200)	(220)		
300ppm I + 20ppm L	0.23	0.30	2.47	6.92	(220)
300ppm I + 20ppm L + 5ppm A	0.88	1.15	0.97	0	(200)

following conclusions were drawn:

- Surface roughness monotonously decreased with the inhibitor and the leveler, whereas surface roughness decreased under low concentration of the accelerator but increased above a critical concentration.
- The dependence of surface roughness on the additives were due to the difference in role between the additives affected the plating rate as follows:
 - the inhibitor: retarding plating rate on the whole surface
 - the leveler: retarding plating rate on sites such as protrusions
 - the accelerator: enhancing plating rate on the valleys
- Residual stress was increased with the inhibitor and the leveler, whereas was decreased with the accelerator.
- The residual stress with organic additives would be explained with the entrapped impurity model rather than elastic strain energy with preferred plane. Future works such as analysis of the plated copper film are accomplished to approve the entrapped impurity model.

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References

1. J. D. Reid, *Plating and Surface Finishing*, **74**, 66 (1987).
2. L. Bonou, M. Eyraud, R. Denoyel, and Y. Massiani, *Electrochimica Acta*, **47**, 4139 (2002).
3. J. J. Kelly, C. Tian, and A. C. West, *Journal of Electrochemical Society*, **146**, 2540 (1999).
4. J. J. Kelly and A. C. West, *Journal of Electrochemical Society*, **145**, 3472 (1998).
5. M. Hayase, M. Taketani, K. Aizawa, T. Hatsuzawa, and K. Hayabusa, *Electrochemical and Solid-State Letters*, **5**, C98 (2002).
6. M. Eyraud, S. Kologo, L. Bonou, and Y. Massiani, *Journal of Electroceramics*, **16**, 55 (2006).
7. L. Mirkova, and St. Rashkov, *Journal of Applied Electrochemistry*, **24**, 420 (1994).
8. Y. Y. Lee, Y. J. Park, J. B. Lee, and B. W. Cho, *Journal of the Korean Electrochemical Society*, **5**, 153 (2002).
9. K. Kondo, N. Yamakawa, Z. Tanaka, and K. Hayashi, *Journal of Electroanalytical Chemistry*, **559**, 137 (2003).
10. T. P. Moffat, J. E. Bonevich, W. H. Huber, A. Stanishevsky, D. R. Kelly, G. R. Stafford, and D. Josell, *Journal of the Electrochemical Society*, **147**, 4524 (2000).
11. M. Tan and J. N. Harb, *Journal of the Electrochemical Society*, **150**, C420 (2003).
12. J. J. Kim, S. K. Kim, and Y. S. Kim, *Journal of Electroanalytical Chemistry*, **542**, 61 (2003).
13. D. R. Turner, G. R. Johnson, *Journal of the Electrochemical Society*, **109**, 798 (1962).
14. V. A. Vas'ko, I. Tabakovic, S.C. Riemer, and M.T. Kief, *Microelectronic Engineering*, **75**, 71 (2004).
15. M. Schlesinger and M. Paunovic, *Modern Electroplating*, p.56, Wiley-Interscience, 2000.
16. G. R. Stafford and C. R. Beauchamp, *209th Meeting Electrochemical Society*, p.430, The Electrochemical Society, Denver (2006).
17. C. H. Lee and C. O. Park, *Japanese Journal of Applied Physics Part I*, **42**, 4484 (2003).
18. H. M. Choi and S. K. Choi, *J. Vac. Sci.*, **A16**, 3348 (1998).
19. H. Lee and S. S. Wong, *Journal of Applied Physics*, **93**, 3796 (2003).
20. S. H. Brongersma, E. Kerr, I. Vervoort, A. Saerens and K. Maex, *Journal of Materials Research Society*, **17**, 582 (2002).
21. R. Walker, *Electrochimica Acta*, **13**, 1861 (1968).
22. K. Pantleon, J. A. D. Jensen and M. A. J. Somers, *Journal of the Electrochemical Society*, **151**, C45 (2004).
23. H. Wendrock, W. Bruckner, M. Hecker, T. G. Koetter and H. Schloerb, *Microelectronics Reliability*, **40**, 1301 (2000).
24. G. G. Stoney, *Proceedings of the Royal Society of London*, **172**, A82 (1909).
25. R. Weil, *Plating*, **57**, 1231 (1970).
26. S. H. Brongersma, E. Kerr, I. Vervoort, A. Saerens and K. Maex, *J. Mater. Res.*, **17**, 582 (2002).