

Diallylamine levelers side chains effect on copper via filling

Yasutaka Yamada, Kazuo Kondo, Minoru Takeuchi*,
Takeyasu Saito, Naoki Okamoto, Masaru Bunya* and
Masayuki Yokoi

Department of Chemical Engineering,
Osaka Prefecture University

1-1, Gakuen-chyo, Sakai, Osaka, 599-8531, Japan

Ph/Fax +81-72-254-9304

* Nittobo Medical Co., Ltd., 2-4-1, Kojimachi, Chiyoda-Ku,
Tokyo 102-0083, Japan

E-mail: kkondo@chemeng.osakafu-u.ac.jp

1. Introduction

Copper via filling of printed circuit board (PCB) stacking technique is a key technology for the development of electronic equipment in the next generation. At present, a lot of additives — PEG, SPS, JGB, Cl⁻ etc — is often used within the copper sulfate plating bath. However the control of the additive's concentration is very difficult. We focused on diallylamine levelers which are expected as single additive. In this study, we examined the diallylamine adsorption behavior by changing structures and a relation between the basic and electrodeposition by changing length and functional group of side chains.

2. Experimental

The bath composition is CuSO₄·5H₂O; 130 g/L, H₂SO₄; 200 g/L. 1 ppm diallylamine was individually added to the electrodeposition bath. Current density was 10 mA/cm². In QCM measurement, 50 ppm diallylamine was added for the sensitivity of adsorption amount. Electrochemical measurement was also performed 10 mA/cm² with platinum rotating disk electrode.

3. Result

1. Figure 1 shows the cross sections by an optical microscope with 60 minute electrodeposition time. Cross sections of Long side chain additive (a) P(DAEPDA[2HCl]/SO₂) and (b) P(DAAHPTA[HCl]/SO₂) are good because their outside film thickness is thin (see arrow). On the other hand in the case (c) P(DAEDA[2HCl]/SO₂) and (d) P(DAEEEDA[2HCl]/SO₂), they are very thick.

2. Figure 2 shows QCM measurements for additive's adsorption. The adsorption order is additive (a) > (b) > (c) > (d). Additives (a) and (b) show thin outside than additive (c) and (d) and this shows good correspondence with QCM measurements.

3. Figure 3 shows the galvanostatic measurements. The electrolyte flow rate at the outside is faster than at the bottom. The high rotation rate of RDE corresponds to the outside and the low to the bottom. The overpotential values at the low speed show almost same but they at the high speed are additive (a) > (b) > (c) > (d). The galvanostatic measurements correspond to the adsorption amount by QCM measurements.

4. Table 1 shows each pKa value of diallylamine. pKa of additive (a) and (b) which show good cross section is higher than that of additive (c) and (d). This is because amine can easily protonate and charge positively with high pKa.

5. Figure 4 shows the diallylamine adsorption model. Initially, chloride ions specifically adsorb onto the electrode surface. Then, positive charging diallylamines adsorb with chloride ions. In this study, the cross sections and QCM adsorption amount are different results because of positive charging amount.

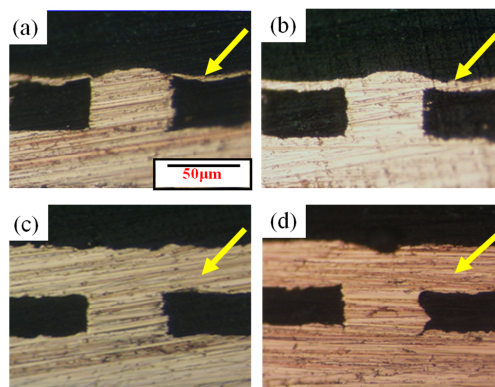


Fig. 1 Cross sectional views of Cu deposited films.

(a) P(DAEPDA[2HCl]/SO₂) (b) P(DAAHPTA[HCl]/SO₂)
(c) P(DAEDA[2HCl]/SO₂) (d) P(DAEEEDA[2HCl]/SO₂)

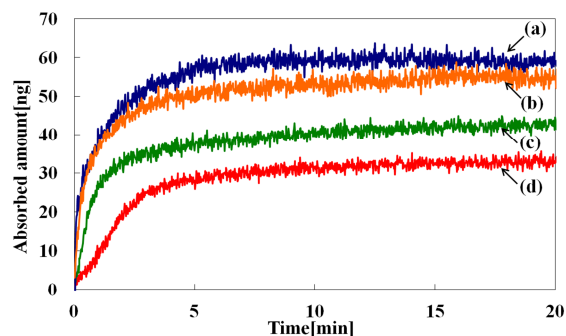


Fig. 2 QCM analyses with diallylamine system additives.

(a) P(DAEPDA[2HCl]/SO₂) (b) P(DAAHPTA[HCl]/SO₂)
(c) P(DAEDA[2HCl]/SO₂) (d) P(DAEEEDA[2HCl]/SO₂)

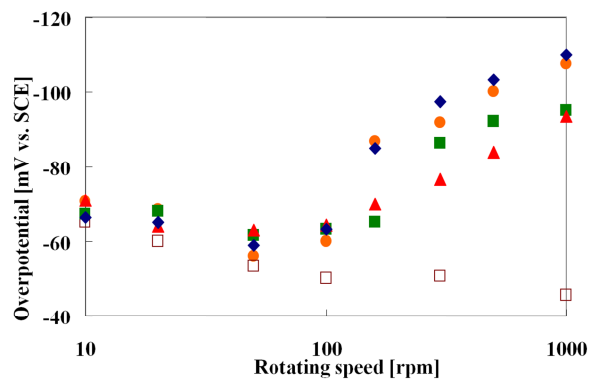


Fig.3 The relation of rotating speed and overpotential with galvanostatic measurement.

(a) P(DAEPDA[2HCl]/SO₂) (b) P(DAAHPTA[HCl]/SO₂)
(c) P(DAEDA[2HCl]/SO₂) (d) P(DAEEEDA[2HCl]/SO₂)

Table 1 The value of pKa of diallylamine system additives.

Additives	pKa
(a) P(DAEPDA[2HCl]/SO ₂)	5.90
(b) P(DAAHPTA[HCl]/SO ₂)	5.49
(c) P(DAEDA[2HCl]/SO ₂)	4.45
(d) P(DAEEEDA[2HCl]/SO ₂)	3.93

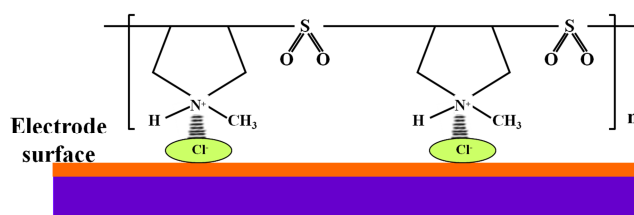


Fig.4 The electrode adsorption model of diallylamine.