

Short Communication

Through-Hole Filling by Copper Electroplating Using Sodium Thiazoliny-Dithiopropene Sulfonate as the Single Additive

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The adsorption behavior of thiazoliny-S-Cu and sodium thiazoliny- dithiopropene sulfonate(SH110) on the copper surface was investigated using molecular dynamics (MD) simulation and atomic force microscope (AFM). The electrochemical behavior of SH110 was evaluated and SH110 was used as the single additive in the through-hole (TH) electroplating. The results indicate that SH110 is an effective additive used for TH filling. Thiazoliny-S-Cu and SH110 could be adsorbed on copper surface. The adsorption behavior of SH110 on copper surface indicates that SH110 is a combination of accelerator and inhibitor. SH110 can be used as an inhibitor at the surface with strong convection, whereas it can be used as an accelerator at the surface with weak convection. The combined approach of experiments and MD simulation can provide an insight into the mechanism of SH110 for TH filling.

Keywords: Through-hole filling; Additive; Sodium thiazoliny-dithiopropene sulfonate; Molecular dynamics simulation.

1. INTRODUCTION

Recently, electronic products are becoming lighter, smaller, thinner, and faster. Accordingly, multilayer printed circuit boards (PCBs) with high-density interconnection(HDI) are necessary for the fabrication of these products[1,2]. The interconnection between two conducting layers on PCB is normally connected by means of copper electroplated micro-vias or through-holes (THs)[3,4]. TH filling by copper electroplating has been one of the most important technologies in the fabrication of multilayer-PCBs[5]. The different current distribution in the TH will give rise to a void at the center of the TH using traditional electroplating method[6,7]. Recently, a copper electroplating technique, namely the butterfly technique (BFT)[5], was developed to achieve the void-free filling of TH. In the BFT, the fastest copper deposition occurs at the center of the TH to form a copper deposit in the shape

of butterfly wings. It has been reported that using additives is an effective method to achieve BFT[5]. The additive system used for PCB electroplating generally contains several additives (i.e., accelerator, inhibitor and leveler)[2,3].

One of the main problems of the additive system is the different consumption rate of each additive. So it will be meaningful by using a single additive instead of the additive system. Wei-Ping Dow et al. achieved BFT using nitrotetrazolium blue chloride as an inhibitor under low current density[5]. The purpose of the present investigation is to achieve BFT and TH filling using a single additive under a relatively larger current density. Molecular dynamics (MD) simulation is one of the most appropriate methods to investigate the interaction between molecules and the metal surface[8,9]. MD simulations also provide a useful tool to interpret the experimental results[10,11]. The combined approach of experiments and MD simulation, used in present investigation, was used to study the possibility using sodium thiazolinyldithiopropane sulfonate (SH110) as the single additive in the TH filling.

2. EXPERIMENTAL

2.1 Molecular dynamics simulation

MD simulation of the interaction between thiazolinyldithiopropane sulfonate (SH110) and the copper surface was carried out in a simulation box (2.045 nm × 1.534 nm × 4.486 nm) with periodic boundary conditions using Materials Studio (from Accelrys Inc). The MD simulation was performed at 297 K, NVT ensemble and CVFF force-field[12], with a time step of 1 fs and simulation time of 1 ns. The interaction energy $E_{\text{surface/thiazolinyldithiopropane sulfonate}}$ between copper surface and thiazolinyldithiopropane sulfonate was calculated as:

$$E_{\text{surface/thiazolinyldithiopropane sulfonate}} = E_{\text{complex}} - E_{\text{surface}} - E_{\text{thiazolinyldithiopropane sulfonate}} \quad (1)$$

with E_{complex} being the total energy of the copper crystal together with the thiazolinyldithiopropane sulfonate, E_{surface} and $E_{\text{thiazolinyldithiopropane sulfonate}}$ being the total energy of the copper crystal and free thiazolinyldithiopropane sulfonate, respectively. The binding energy was the negative value of the interaction energy, $E_{\text{binding}} = -E_{\text{surface/thiazolinyldithiopropane sulfonate}}$.

2.2 Surface morphology analysis

AFM measurements were used to study the adsorbed layer of SH110 on the copper surface. Sections with size of 10mm×10mm cut from the PCB were mechanically polished, then cleaned and dried. A cleaned and dried copper surface was obtained from the PCB. The prepared PCB sections were immersed in the 20ppm SH110 aqueous solution for 20min. The immersed sections were rinsed with deionized water and then dried. These PCB sections were used for AFM tests.

2.3 Electrochemical evaluation and TH filling

Electrochemical tests were performed in a three-electrode cell using a potentiostat/galvanostat (PARSTAT2273) at 24°C. A copper rotating disk electrode (Cu-RDE) was employed as the working

electrode. The counter electrode was a platinum plate. A saturated mercurous sulfate electrode(SSE) was used as the reference electrode.

PCB fragments with many THs were electroplated at a current density of $0.6\text{A}/\text{dm}^2$ at $24\pm 1^\circ\text{C}$. The diameter and depth of the TH were $200\mu\text{m}$ and 1mm , respectively. Details in the electroplating process was reported in the previous work[13]. Basic bath was composed of $60\text{g}/\text{L}$ $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, $230\text{g}/\text{L}$ H_2SO_4 and $50\text{mg}/\text{L}$ Cl^- . SH110 was used as the additive. The performance of TH plating was evaluated from the cross-sectional pictures obtained by a metaloscope.

3.RESULTS AND DISCUSSION

3.1 Interaction between the additive and the copper surface

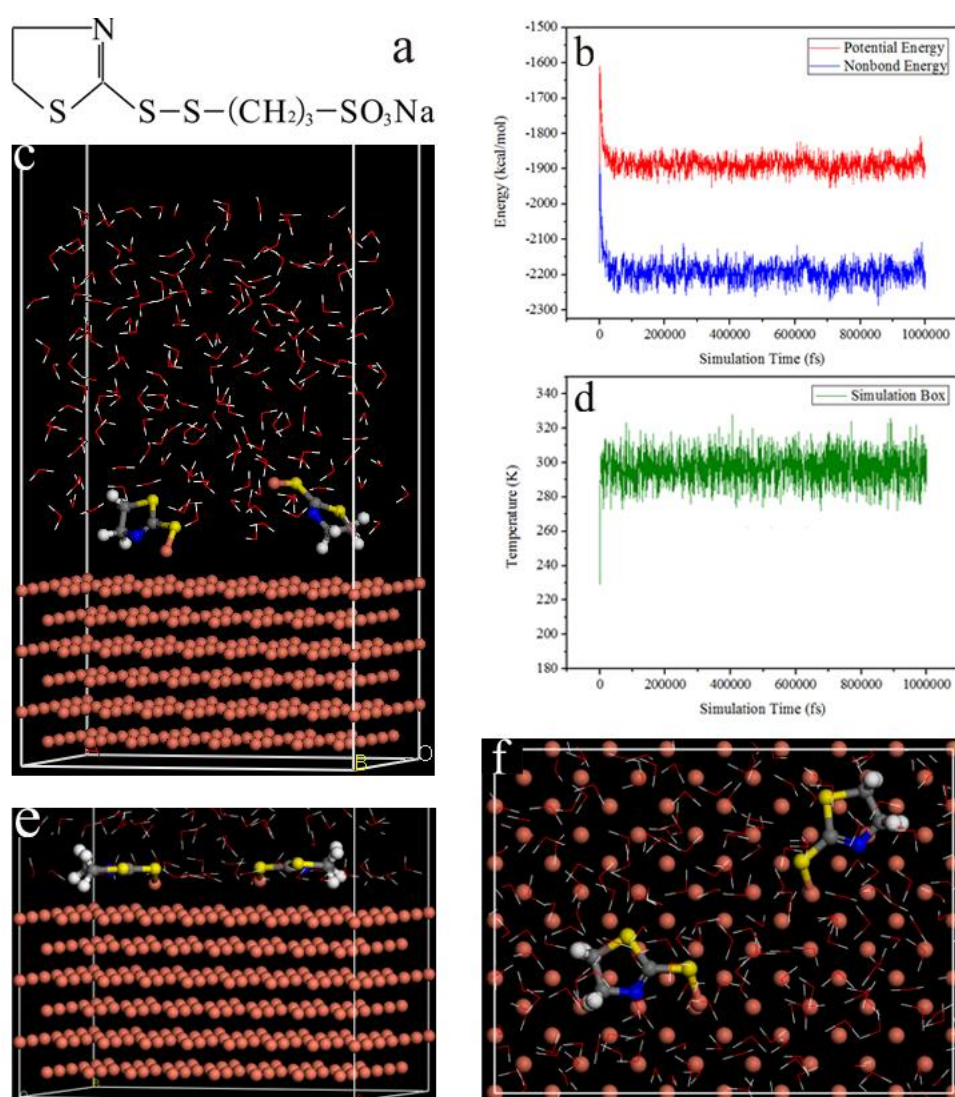


Figure 1. (a) Molecular structure of SH110. (b), (d) Energy and temperature fluctuation curves of the MD simulation. (c) Initial configuration of the simulation box (thiazolinyl-S-Cu and copper visualized by balls and sticks, water molecules visualized by lines). (e), (f) Side and top view of the final equilibrium configuration of the simulation box.

It has been reported that the disulfide bond in the accelerator molecule disconnected in the electroplating process[14]. The disconnected disulfide bond can be combined with Cu(I)[15]. Therefore SH110, shown in Fig.1a, can be decomposed into two molecular fragments: thiazoliny-S-Cu and Cu-S-propane-sulfonate. The molecular fragment of Cu-S-propane-sulfonate is an accelerator in the copper electroplating which has been investigated clearly[15]. MD simulation was performed to study the adsorption behavior of thiazoliny-S-Cu on Cu(001) surface. The thiazoliny-S-Cu in the initial configuration, shown in Fig.1c, was placed close to the copper surface randomly. Energy and temperature fluctuation curves, shown in Fig.1b and d, indicated that the simulation system was finally at equilibrium. E_{binding} , calculated from Fig.1e, was 377.64 kJ/mol. It meant that thiazoliny-S-Cu could be adsorbed on the copper surface. Moreover, the thiazoline-ring in thiazoliny-S-Cu was approximately parallel to the copper surface. Therefore, thiazoliny-S-Cu could prevent the deposition of Cu(II) on the cathode. The behavior of thiazoliny-S-Cu is similar to an inhibitor or leveler[2].

Fig.2a and b showed the polished and cleaned copper surface. It can be seen that there were trenches which derived from the polishing process. Compared with the untreated copper surface, the copper surface treated with SH110 solution, shown in Fig.2c and d, showed a completely different morphology. Angular trenches were not existed, which can be considered that the adsorbed layer of SH110 on the copper surface changed the morphology.

Results of the MD simulation and AFM images showed that thiazoliny-S-Cu and SH110 could be adsorbed on the copper surface, which indicated that SH110 was a combination of accelerator and

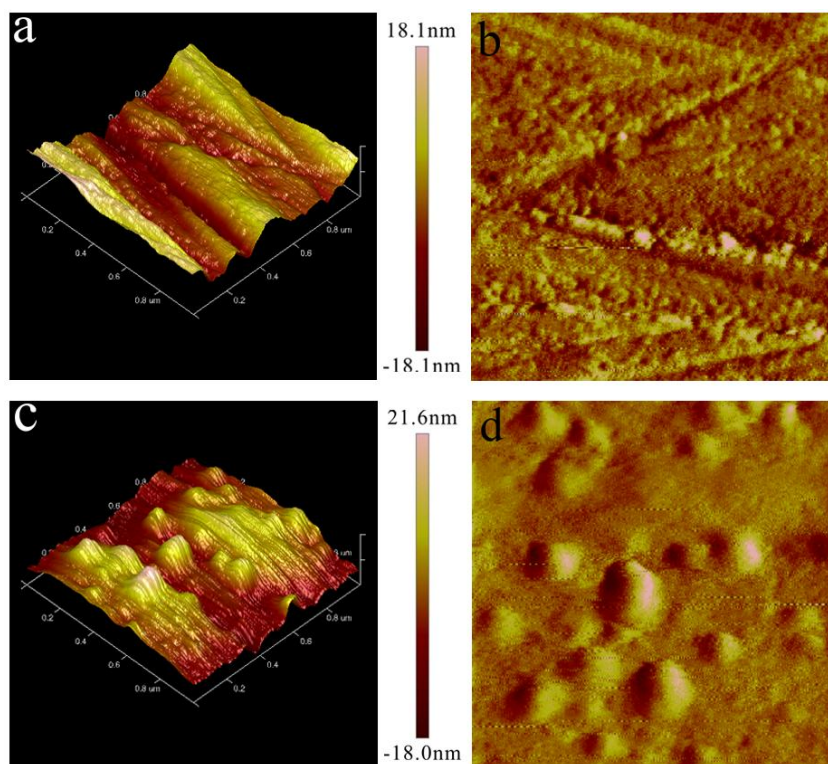


Figure 2. (a), (b) AFM 3D height and deflection image of the polished copper surface. (c), (d) AFM 3D height and deflection image of the copper surface treated with SH110.

inhibitor. If accelerator-fragments (Cu-S-propane- sulfonate) and inhibitor-fragments (thiazoliny1-S-Cu) have different concentration distribution at the mouth and the center of the TH under certain conditions, the BFT and filling of the TH may be achieved using SH110 as the single additive.

3.2 Electrochemical evaluation

E-t curves, measured at the current density of $0.6\text{A}/\text{dm}^2$ going with the addition of SH110 at 500s were shown in Fig.3a. The potential difference, $\Delta\eta$, defined by $\Delta\eta = \eta(100\text{rpm}) - \eta(1000\text{rpm})$, was used to characterize the different inhibition of copper electrodepositon at 100 and 1000rpm[2].

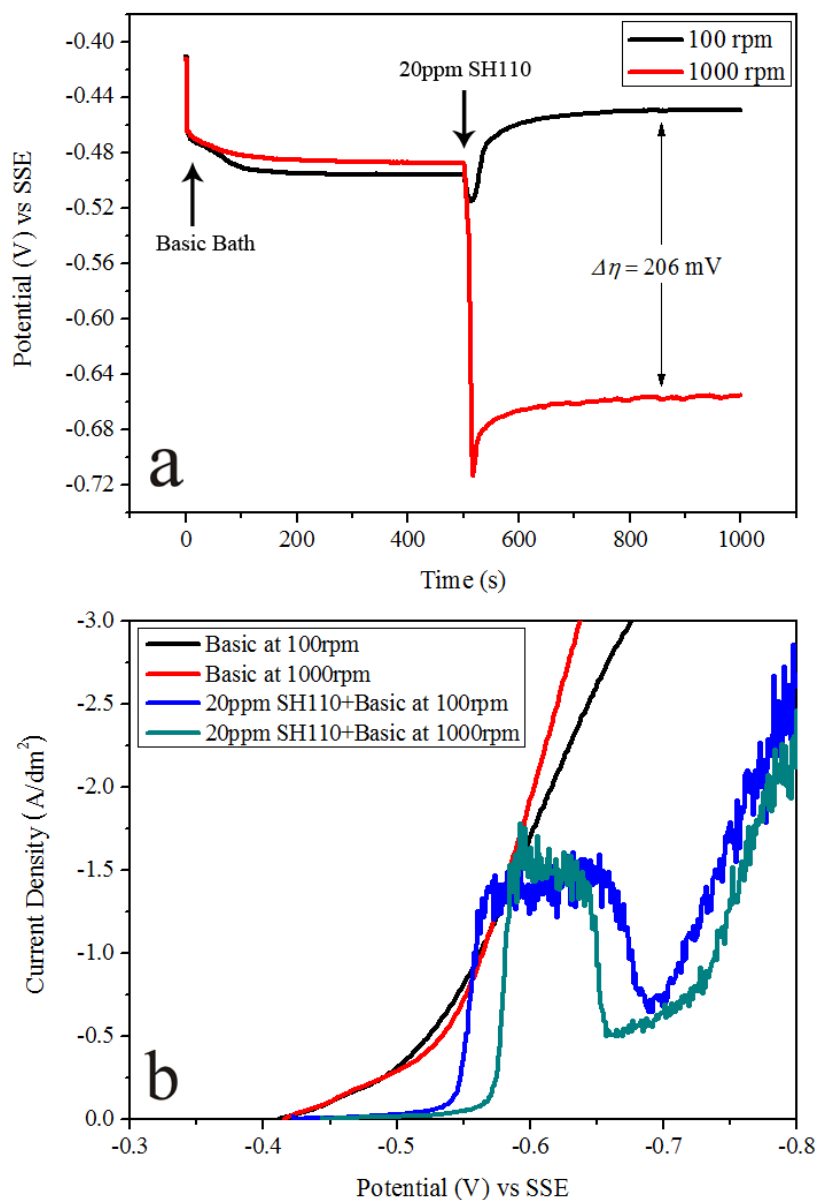


Figure 3. (a) E-t curves at the current density of $0.6\text{A}/\text{dm}^2$ at different rotation speeds. (b) Potentiodynamic polarization curves of different formulae at different rotation speeds.

The cathodic potentials both at 100 and 1000rpm increased suddenly when 20ppm SH110 was added at 500s, which could be attributed to the adsorption of SH110 on the cathodic surface. Moreover, the increase of the cathodic at 1000rpm was greater than that at 100rpm. This indicated that stronger convection gives rise to stronger inhibition of copper electrodeposition. As time goes on, the decomposed Cu-S-propane-sulfonate decreased the cathodic potential. An important phenomenon appeared after the cathodic potentials were finally stable. The final cathodic potentials showed that the addition of 20ppm SH110 decreased the cathodic potential at 100rpm, whereas it increased the cathodic potential at 1000rpm. In other words, 20ppm SH110 was used as an accelerator at 100rpm, whereas it was used as an inhibitor at 1000rpm. The electrodeposition rate of copper at the center(weak convection) of the TH will be increased, whereas the electrodeposition rate at the mouth(strong convection) will be decreased.

Potentiodynamic polarization curves of different formulae measured at 100 and 1000rpm were given in Fig.3b. Significant reductive currents appeared at about -0.42V vs SSE using the basic bath. In contrast, significant reductive currents appeared at about -0.55 and -0.58V vs SSE at 100 and 1000rpm using the bath containing 20ppm SH110. SH110 inhibited the appearance of the reductive currents. Moreover, the inhibition at 1000rpm was stronger than that at 100rpm. It indicated that stronger convection gives rise to stronger inhibition, which is consistent with the results of E-t curves. As the increase of cathodic scan potentials, the reductive currents of the bath containing SH110 increased rapidly. According to the previous analysis, the increase of the current was attributed to the decomposed Cu-S-propane-sulfonate. A current platform appeared when the currents increased to about $1.3\text{A}/\text{dm}^2$. Moreover, curves were fluctuant. This was attributed to the interaction or competition between the accelerator-fragment and the inhibitor-fragment. As the continue increase of cathodic scan potentials, the reductive current decreased rapidly. It was because that more and more decomposed thiazolanyl-S-Cu adsorbed on the cathodic surface. Moreover, the cathodic currents at 100 and 1000rpm began to decrease at -0.67 and -0.65V vs SSE, respectively. This indicated that more inhibitor-fragments were adsorbed on the cathodic surface with stronger convection. These electrochemical behaviors provide favorable conditions for the TH filling using SH110 as the single additive.

3.3 Through-hole filling

The convection at the mouth and the center of the TH is not necessarily equal to 1000 and 100rpm in the actual TH electroplating process. Therefore the SH110 concentration used in the TH filling may not be 20ppm. However, according to the analysis of the electrochemical behavior SH110, there should be a concentration or concentration range of SH110 to achieve BFT. The typical results of TH electroplating using electroplating bath with and without 10ppm SH110 were shown in Fig.4.

It can be seen from Fig.4d that the fastest copper deposition occurred at the center of the TH when 10ppm SH110 was present in the electroplating bath. A void, shown in Fig.4c, was formed in the TH filling process using the basic bath. However, the TH filling without a void in the center was

achieved using 10ppm SH110 as the additive. It indicated that SH110 can be used as the single additive for BFT and TH filling.

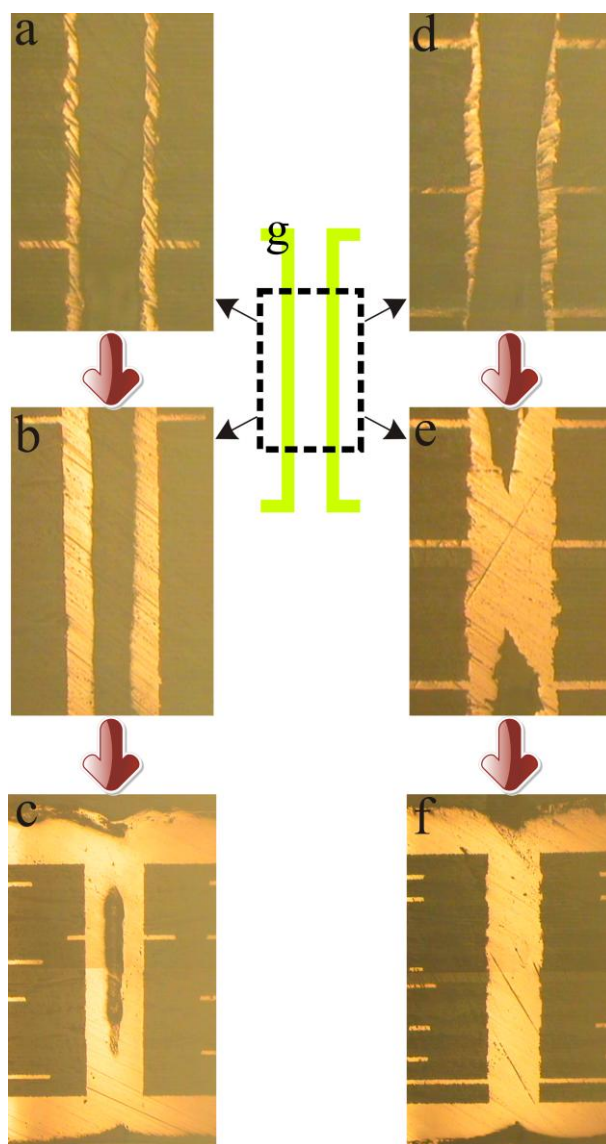


Figure 4. (a), (b) and (c) Cross-sectional pictures of the TH obtained from the basic bath. (d), (e) and (f) Cross-sectional pictures of the TH obtained from the bath containing 10ppm SH110. (a), (d) electroplating for 3h. (b), (e) electroplating for 10h. (c), (f) electroplating for 18h. (g) Model of the TH.

4. CONCLUSION

The MD simulation showed that the decomposed thiazoliny-S-Cu could be adsorbed on copper surface. Moreover, thiazoline-ring in SH110 was approximately parallel to the copper surface. An adsorbed layer could be formed on the copper surface when the copper surface was immersed in the SH110 solution. The thiazoliny-S-Cu can be considered as an inhibitor, therefore SH110 is a

combination of accelerator and inhibitor. SH110 can inhibit the copper electrodeposition at the surface with strong convection, whereas it can accelerate the copper electrodeposition at the surface with weak convection. The TH filling without a void at the center of the TH was achieved using 10ppm SH110 as the single additive.

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