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Investigation of Through-Hole Copper Electroplating with Methyl Orange as A Special Leveler

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Abstract: Methyl Orange (MO) with two kinds of functional groups can act as both an accelerator and an inhibitor, which has been used as a special leveler to simplify the electroplating additive system in the through-hole (TH) copper electroplating experiments. In this work, the role of MO in TH electroplating is characterized by molecular dynamics simulations and quantum chemical calculations. It is suggested that MO can spontaneously flatten the copper surface and be well adsorbed on the cathode surface, which inhibit the copper electrodeposition on the cathode. Electrochemical behavior of MO was evaluated by galvanostatic measurements (GM) and cyclic voltammetry (CV) to confirm that MO hardly affects the potential due to its duel functions of depolarizing and polarizing effects from the molecular structure of sulfonic acid group and other groups to achieve the internal Cu^{2+} reduction acceleration and mass transfer inhibition. Throw power value of TH with the aspect ratio of 10:1 could reach 92.34% from the base plating solution bath with the additions of only EO/PO and MO. The study of MO could provide new ideas for the development of electroplating additive system.

Key words: copper electroplating; through-hole; additive; methyl orange

1 Introduction

Electroplating copper technology greatly affects the development of electronic interconnection of multilayer printed circuit boards (PCB). The acidic sulfate basic plating solution is composed of copper sulfate and sulfuric acid. Electroplating in the plating solution without any additives can only form a rough and no bright copper coating. Additives play an important role in the plating solution because they greatly affect the plating thickness at the mouth and the center in the through-hole (TH)[1]. The additive system generally includes accelerator, inhibitor and leveler. Under the synergistic of chloride ions, sulfonic acid group of most accelerators accelerates copper deposition at the center in the TH[2]. According to existing researches, the accelerator with sulfonic acid groups can capture positively charged Cu^{2+} in solution by electrostatic interaction, and then can rapidly reduce Cu^{2+} to Cu^0 by synergistic action with Cl^-.

Janus Green B (JGB) as a widely used leveler exhibits nitrogen-nitrogen double bond to inhibit copper deposition[2]. Early works have reported the synthesis of a new additive to obtain a good leveling effect during copper electroplating. Ding et al.[3] synthesized a

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Received: 2022-03-04; Revised: 2022-04-10. *Corresponding author, Tel: (86)18980602785, E-mail: ymchen@uestc.edu.cn new leveling agent TS-L to increase throw power (TP) with the increase in the concentration of TS-L. When 50 mg·L^{-1} TS-L, 10 mg·L^{-1} brightener and 600 mg·L^{-1} inhibitor were added to the plating solution, TP value reached 87% in the condition of TH with the aspect ratio (AR) of 6.4:1. Zheng et al.[4] synthesized a new leveling agent VIBDGE. When the concentration of VIBDGE was 10 mg·L^{-1}, the TP increased to 90.0% for the TH with the aspect ratio of 6.4:1. In addition, some new levelers have been found to improve the quality of TH interconnection[5]. Wang et al.[2] proved through a series of experiments that Safranine T (ST) could not play a leveling role like JGB although the structure of ST was similar to that of JGB. Li et al.[6] proposed a subversive view that JGB would be adsorbed on copper through its -N=N- bond after studying the adsorption process of JGB during copper deposition using the methods of mass spectrometry and nuclear magnetic resonance. Tao et al.[7] obtained an optimal plating solution composed of $CuSO_4$, H_2SO_4, chloride ions, propylene oxide ethylene oxide propylene oxide (PEP), 3-mercaptopropyl sulfonate (MPS) and JGB, and the microvia could be fully filled using the plating formula.

Because of the special structure of MO, accelerator and leveler can be replaced in electroplating solution, thereby, simplifying the electroplating additive system. In this paper, this idea was confirmed through electroplating experiments, electrochemical tests, and simulations. Through the use of MO, a uniform copper deposition was successfully obtained for TH with the aspect ratio (AR) of 10:1.

2 Experimental

2.1 TH Electroplating

Rectangular PCB fragments of 50 mm × 150 mm with TH were used herein as the test samples for electroplating. The aspect ratio (AR) of TH was 10:1. The fragments were metallized by electroless copper plating and pre-plated for 3 μm before the electroplating. The PCB fragments were electroplated at a current density of 1.2 A·dm^{-2} for 60 min in a cell with 1.5 L electroplating bath at 25 ℃. A continuous flow of air bubbles at 2.5 L·min^{-1} was used for constant agitation in order to ensure the good mass transfer.

Basic bath was composed of 75 g·L^{-1} $CuSO_4\cdot 5H_2O$, 240 g·L^{-1} H_2SO_4 and 60 mg·L^{-1} Cl^-. Ethylene oxide and propylene oxide block copolymers (EO/PO) were used as the inhibitor, while MO was employed for the special leveler. 200 mg·L^{-1} EO/PO and 6 mg·L^{-1} MO as additives were added into basic bath for the systematic experiment. The thickness of the electroplated copper in TH was evaluated from the cross-sectional pictures using a metallographic microscope (ASIDA-JX23RT, Zhengye Technology). *TP* value was used to characterize the thickness uniformity of the plating in the TH, as defined in Equation (1) as:

$$TP=\frac{2\times(\delta_e+\delta_f)}{\delta_a+\delta_b+\delta_c+\delta_d}\times 100\% \qquad (1)$$

where δ_a, δ_b, δ_c and δ_d are the plating thicknesses at the surface of TH, δ_e and δ_f are the plating thicknesses at the center of TH in Figure 1.

2.2 MO Simulations and Electrochemical Test

The Forcite module in molecular dynamics simulations is used to optimize the structure of the constructed adsorption model. The adsorption energy of the additive and the binding energy to the copper surface are calculated.

During molecular dynamics simulations with Materials Studio, the Forcite module is used to optimize the structure of the constructed adsorption model with fixing copper atoms, while the settings of Forcite

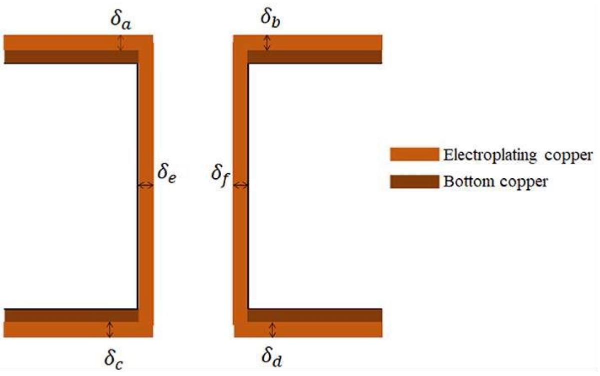

Figure 1 Model of TH with copper electroplating (color on line)

calculation are chosen as COMPASS II for force field and canonical ensemble. After completing the above optimization, the Forcite module is used to perform molecular dynamics simulation for 200 ps with time step of 1 fs at 25 ℃. In this way, the adsorption energy and the binding energy of the additive on the copper surface can be calculated.

Quantum chemical calculations are performed by DMol3 module to illustrate the frontier molecular orbital energies and energy gap of MO. The molecular structure optimization of MO is obtained by DFT method. The frontier molecular orbital energies are consisted of energy of the highest occupied molecular orbital (E_{HOMO}) and the energy the lowest unoccupied molecular orbital (E_{LUMO}). The energy gap (ΔE) should be calculated by Equation (2)[8].

$$\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} \tag{2}$$

All of the electrochemical tests were performed in a three-electrode cell using a potentiostat/galvanostat (PARSTAT2273, Switzerland Metrohm) at 25 ℃. A platinum rotating disk electrode (Pt-RDE) with a diameter of 5 mm was employed as the working electrode. The counter electrode was a platinum plate with an area of 1 cm^2. A saturated mercurous sulfate electrode (SSE) was used as the reference electrode. Cyclic voltammetric (CV) testing was completed in the sweep potential ranging from -0.7 V to 0.1 V. Galvanostatic potential transient measurements (GM) were completed using Pt-RDE at rotation speeds of 1000 $\mathrm{r \cdot min^{-1}}$ and 100 $\mathrm{r \cdot min^{-1}}$.

The contact angle was measured by the contact angle tester (JY Pha, Zhengye Technology) to analyze the quantitative liquid droplets on the copper surface, and the hydrophilic and hydrophobic properties of the copper surface are reflected by the size of the contact angle[9].

3 Results and Discussion

3.1 Function of MO in TH Electroplating

The results of the TH electroplating for 10:1 TH using different electroplating baths are shown in Figure 2. The TP with AR of 10:1 was only 56.59% using the basic electroplating bath. The TP of 10:1 TH was 72.61% using the bath containing 200 $\mathrm{mg \cdot L^{-1}}$ EO/PO. When only EO/PO was added, the plating thicknesses at the center and the surface of the TH both increased significantly. However, the increase magnitude of copper thickness on the surface was lower than that at the center. The TP value increased to 92.34% using the bath containing 200 $\mathrm{mg \cdot L^{-1}}$ EO/PO and 6 $\mathrm{mg \cdot L^{-1}}$ MO. Obviously, the plating copper thickness on the surface of TH from the basic bath with EO/PO and MO is smaller than that from the basic bath with only EO/PO, but the plating copper thickness at the center of TH from basic bath with

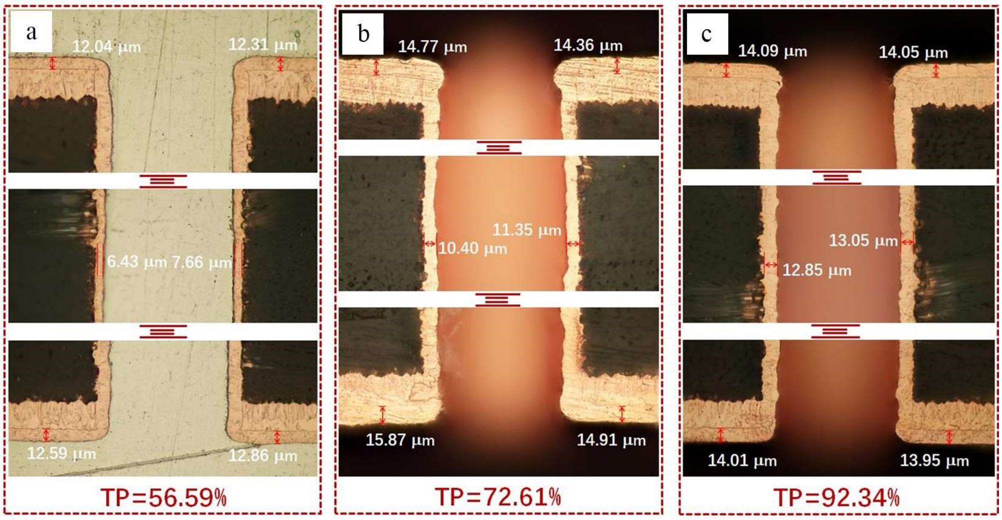

Figure 2 Cross-sectional pictures of 10:1 TH from the bath (a) without additive and containing (b) 200 $\mathrm{mg \cdot L^{-1}}$ EO/PO; (c) 200 $\mathrm{mg \cdot L^{-1}}$ EO/PO and 6 $\mathrm{mg \cdot L^{-1}}$ MO (color on line)

EO/PO and MO is larger.

3.2 The Role of MO in TH Electroplating

Figure 3 shows the molecular structure of MO. Regarding the adsorption of MO on the copper surface, it is likely to be related to the nitrogen-nitrogen double bond and the sulfonic acid group just like JGB that would be adsorbed on copper through -N=N- bond during copper deposition.

The adsorption model of MO is shown in Figure 3. It suggests that the MO molecule could spontaneously flatten on copper surface just like JGB molecule[12]. The adsorption energy of MO molecule and copper surface is calculated to be -86.28 kcal·mol^{-1}. It indicates that MO can be adsorbed on the copper surface, compared to the case for the levelers of JGB[12] and VIBDGE[4].

Contact angles were tested to investigate the additive adsorption function for the baths with different additive systems. After the water droplets stayed on the copper surface for 60 s, the contact angles of the plating solutions under various additive systems were measured as shown in Figure 4. Among them, the wettability of the base plating solution without any additives on the copper surface was the worst to reach the contact angle of 67.4° because the copper surface did not contain hydroxyl groups, and the plating solution without additives had poor wettability on the pure copper surface[13]. The wettability of the bath containing only EO/PO was better with the contact angle of 59.7°. The wettability of the bath containing only MO was also better than that of base plating solution with the contact angle of 61.6°. In the plating solution composed of EO/PO and MO, the contact angle was further reduced to 59.3° because EO/PO is a wetting agent to reduce the wettability of the system, thereby, showing a smaller contact angle.

Quantum chemical calculations is employed to obtain some electronic properties and orbital information. The localization of HOMO and LUMO of MO is shown in Figure 5. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between frontier orbitals

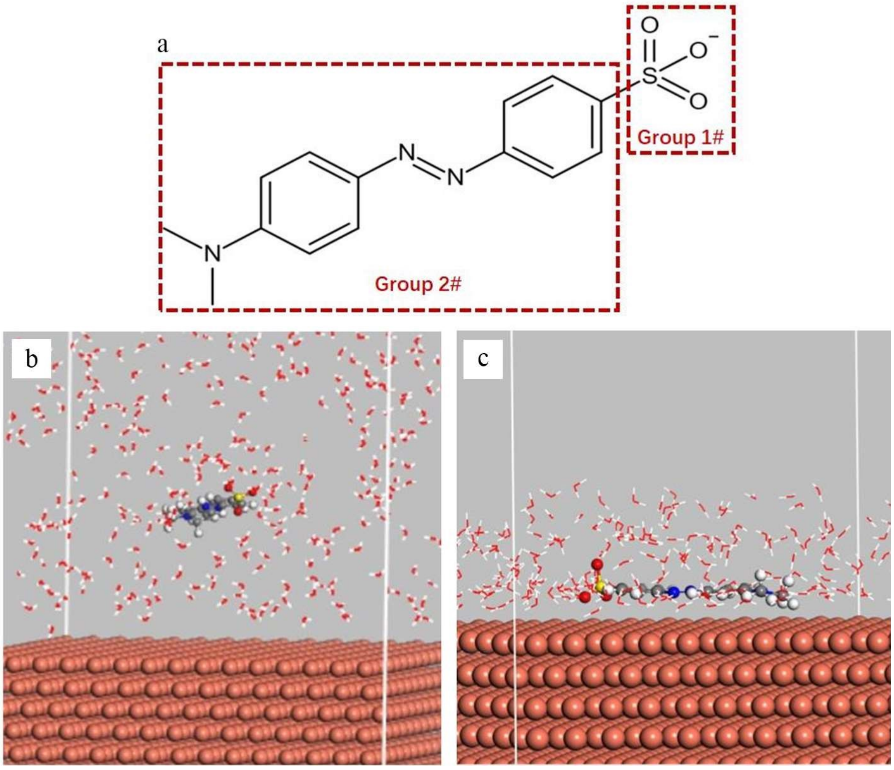

Figure 3 (a) Molecular structure of MO with sulfonate ion defined as Group 1# and other group defined as Group 2#; (b) MO before the adsorption; (c) MO after the adsorption on copper surface (color on line)

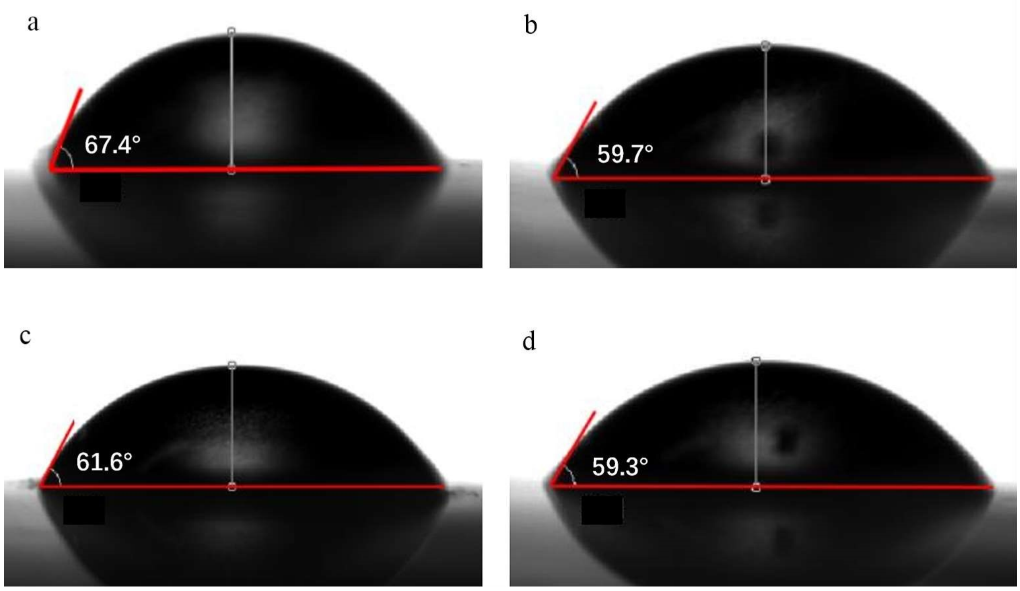

Figure 4 Contact angles of the baths with different additive systems: (a) basic bath; (b) basic bath + EO/PO; (c) basic bath + MO; (d) basic bath + EO/PO + MO (color on line)

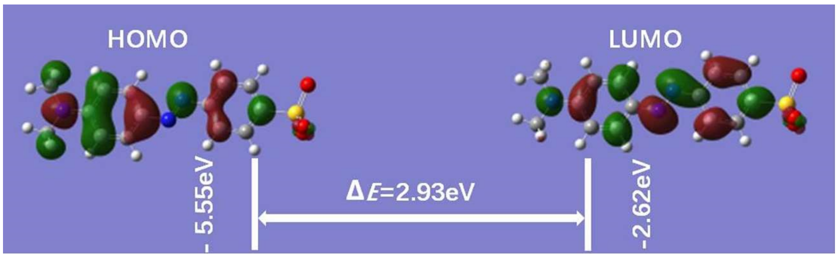

Figure 5 The calculation results of HOMO and LUMO for MO molecule (color on line)

(HOMO and LUMO) of reacting species. The electron donating ability and electron accepting ability are associated with the energy of HOMO and LUMO. HOMO has the highest electron energy and is most likely to change and lose it[10, 11]. LUMO has the lowest energy in the unoccupied orbital and is easier to accept electrons. Therefore, the higher value of E_{HOMO} indicates a tendency of the molecule to donate electrons and the lower value of E_{LUMO} indicates a tendency of the molecule to accept electrons[14]. As the increasing of E_{HOMO} and the decreasing of E_{LUMO}, the binding ability of the organics to the metal surface is stronger. On the other hand, the gap between E_{HOMO} and E_{LUMO} could be used to characterize the binding ability of the organics to the metal surface.

The E_{HOMO} values of JGB and MO are -5.567 eV and -5.548 eV, respectively. It indicates that the electron donating abilities of JGB and MO are similar. On the other hand, MO could be well adsorbed on the cathode surface and inhibit the copper electrodeposition on the cathode. Through the calculation, the ΔE value of MO is 2.93 eV, indicating a stable adsorption structure between MO and copper surface compared to the case for JGB[15].

Figure 6a presents the CV curves under different plating solutions, while Figure 6b is the enlarged view of the curves between -0.40 V to -0.32 V in Figure 6a. After the only addition of MO into the basic bath, the stripping area of copper tended to be a bit decreased, compared to that of the basic bath. Moreover, the only addition of EO/PO in the basic bath induced a dramatical decrease of copper stripping area.

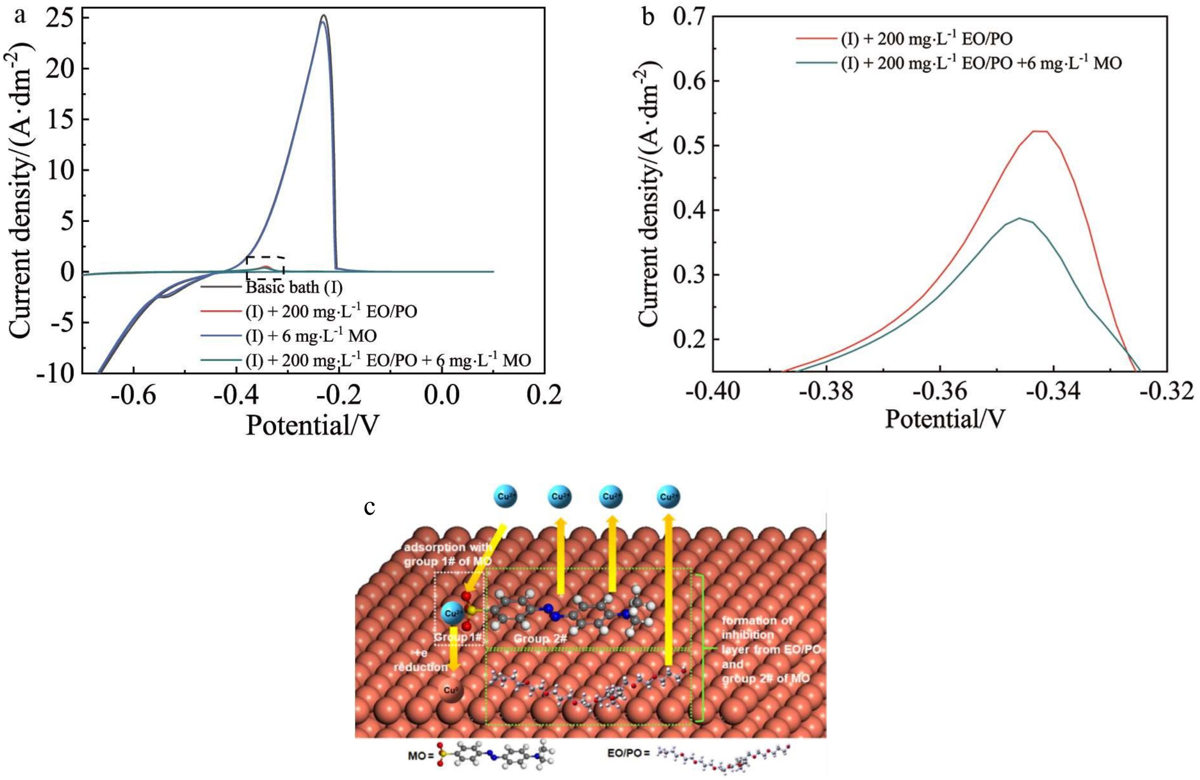

Figure 6 (a) CV curves of different electroplating baths; (b) the enlarged view of the curves between -0.40 V to -0.32 V for Figure 6a; (c) The mechanism of MO in electroplating (color on line)

MO and EO/PO in the basic bath led to a weakened decrease of copper deposition. This could be explained as follows: (1) the group 1# of MO could catch the Cu^{2+} to promote the reduction after obtaining electrons while the group 2# of MO hinders Cu^{2+} to transfer to copper surface; (2) Under the synergy of MO and EO/PO the deposition rate is reduced, and the copper layer becomes uniform. Due to a synergistic effect between MO and EO/PO to promote the deposition rate on the surface, the thickness of copper plating on the surface is reduced from about 15 μm to about 14 μm in Figure 2.

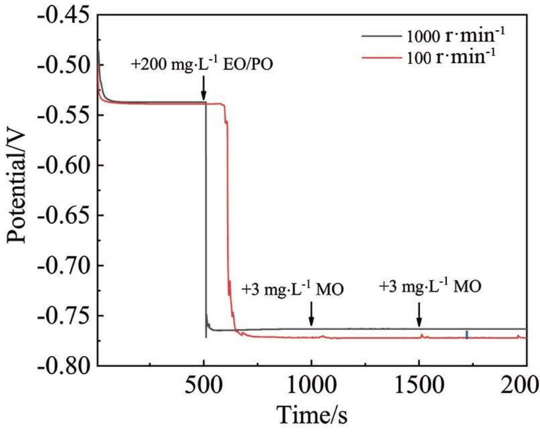

Figure 7 Potential transients of GM with the successive additions of EO/PO and MO in the plating density of 1.2 A·dm^{-2} at adding intervals of about 500 s (color on line)

The GM results at the rotation speeds of 1000 r·min^{-1} and 100 r·min^{-1} are shown in Figure 7. After 200 mg·L^{-1} EO/PO was added at 500 s intervals in the basic bath, the cathodic potential was sharply decreased from -0.535 V to -0.770 V. It supports that EO/PO could strongly inhibit the deposition of copper[14]. Then the adsorption/dissociation of EO/PO gradually reached an equilibrium and stabilized at -0.760 V. This was related to the large binding energy of EO/PO, and the adsorption of EO/PO on the cathode blocked the reactive sites and inhibited the copper deposition. After the potential became stable, 3 mg·L^{-1} MO was added into the bath every 500 s. MO caused a gentle change in potential because MO was formed by simultaneous competition between the group 1# in MO for the Cu^{2+} reduction acceleration and the group 2# in MO for the Cu^{2+} transfer inhibition to the cathode. In addition, the GM results in the conditions of 1000 $r \cdot min^{-1}$ and 100 $r \cdot min^{-1}$ presented respective potentials of -0.763 V and -0.771 V, causing a potential difference of 8 mV because of fast mass transfer to hinder the absorptions of EO/PO and MO on copper surface. Higher potential of the plating solution in the condition of 1000 $r \cdot min^{-1}$ resulted in a little faster Cu^{2+} reduction. In this way, a thick copper plating of about 14.0 μm in thickness was formed at the surface of TH with fast mass transfer and unstable absorptions of EO/PO and MO. On the other hand, gently low mass transfer but good capture of Cu^{2+} from MO could make both inhibition and acceleration of Cu^{2+} reduction with competitive interaction, thereby, leading to the copper plating of about 13.5 μm in thickness inside TH but close to the thickness compared to that at the surface of TH. Above result on copper deposition rate matched well with that displayed in Figure 2c.

4 Conclusions

MO was used as a special leveler in the TH copper electroplating experiments to replace the accelerator and leveler so that the electroplating additive system could be simplified. Results from molecular dynamics simulations showed that the MO molecule could spontaneously flatten on copper surface, and the adsorption energy of MO molecule on copper surface is calculated to be -86.28 $kcal \cdot mol^{-1}$. Result from quantum chemical calculations that ΔE of MO is 2.93 eV suggested that MO could be well adsorbed on the cathode surface. Electrochemical tests of CV and GM demonstrated that MO could simultaneously accelerate and inhibit copper deposition from the molecular structures of sulfonic acid group and other groups, respectively. The additions of EO/PO and MO in the plating solution could contribute to a uniform copper plating in the surface and inside of TH with the aspect ratio of 10:1, leading to good agreement of TP of 92.34%. Thus, MO could be suitable for the development of TH copper electroplating with only two additives.

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特殊整平剂甲基橙在通孔电镀铜的应用

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摘要: 甲基橙具有两种基团,可以同时起到加速和抑制作用,可作为特殊的整平剂应用与通孔电镀铜实验中。通过分子动力学模拟和量子化学计算来表征甲基橙在通孔电镀铜中的作用, 结果表明甲基橙可以很好地吸附在阴极表面并抑制铜的电沉积。通过恒电流测试和循环伏安测试结果显示, 甲基橙由于同时具有磺酸基的去极化和其分子结构部分的极化作用, 形成协同分子内对铜加速还原和阻碍传质的竞争效应, 所以几乎不影响电位。在板厚孔径为 10:1 的通孔电镀铜实验中, 仅以甲基橙和环氧乙烷和环氧丙烷嵌段共聚物作为添加剂, TP 值可达到 92.34%。

关键词: 电镀铜; 通孔; 添加剂; 甲基橙