Effects of Molecular Weight of Organic Additives on the Mechanical Properties of Acid Copper Deposits

C.H. Huang, Chemistry Department, Soochow University, Taipei, Taiwan C.H. Lee, Material Research Laboratories, ITRI, Chutung, Taiwan W.Y. Shu and H.M. Wu, Materials & Electro-Optics Research Division of Chung Shan Institute of Science & Technology, Lung Tan, Taiwan

Owing to the interfacial activity of the acid copper baths was slightly influenced by the molecular weight of organic additives, hence different mechanical properties of the acid copper deposits were obtained. The results of CVS, DSC, and XRD were investigated to explain the effect of molecular weight of organic additives on the mechanical properties of acid copper deposits.

For more information, contact: C.H. Huang

Chemistry Department Soochow University Shih-Lin, Taipei, Taiwan

Phone: +886 02 28819471 Ext. 6804 Fax: +886 02 2592 3627 E-mail: cchhuang@mail.scu.edu.tw

Introduction

It is well known, that special organic additives were added to the copper plating electrolytes to improve the physico-mechanical properties of electrodeposited copper layers. These organic compounds cause a polarization effect and suppress cathodic current at a given voltage, hence changing the crystallite size and/or dispersion of fine impurity particles in the deposits.¹ This may be the reason for the variation of the mechanical strength of the deposits.

Based on an analysis of our published literature data concerning the polyethylene glycol (PEG) and thiourea derivatives it was shown that the suppression of the deposition current increased with increasing the surface activity of the additive.^{2,3} Organic additives with greater surface activity have greater adsorption on the cathode. Therefore, the CVS relative rate parameters (Ar/As) decreased with increasing the surface activity of these additives in the copper electrolyte. Different Ar/As value means different nucleation and growth of copper deposit, resulting in different micro-structures and physico-mechanical properties of the deposit.⁴

However, both of polyethylene glycol (PEG) and thiourea derivatives are somewhat of surface active agents, they only slightly changed the surface tension or contact angle of the copper electrolyte. Further study of these additives, a correlation between the Ar/As values and the molecular weight (MW) of these additives was found. Because of a greater MW of these additives has a greater surface activity, hence the Ar/As values decreases with increasing the MW of these additives. Therefore, MW of these additives plays a fundamental role in determining the physico-mechanical properties of copper deposits. The calculation of MW change is easier than the determination of surface activity change, hence studies have thus focused on the effects of MW of additives in the acidic copper sulfate electrolyte to explain the substantial influence of the MW on physico-mechanical property of copper deposits. The results of studies include electrochemical studies, X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimeter (DSC).

Experimental

Copper deposits were prepared from the copper bath which containing 80 g/L of cupric sulfate (CuSO₄·5H₂O) and 80 g/L of sulfuric acid (H₂SO₄) to which chlorides had been added in the form of HCl to bring the free chloride concentration to a 60 mg/L level. Sodium carboxymethyl cellulose (CMC) was added to the bath to study the MW effect on the mechanical properties of the copper deposits. The average MW of CMC are about 90,000, 250,000 and 700,000, designed CMC9, CMC25, and CMC70, respectively. Electroplating was conducted on bright, flat, 2.5 x 14 cm stainless steel specimens in 2 liter solution from 3 to 9 A/dm² at 25° C, using 5 x 11 cm platinum anode. The solution agitated with propeller blades at 120 rpm. When the deposit reached the required thickness of around 35 µm, the deposited layer was separated mechanically. Owing to the work has a higher sulfuric acid concentration in the electrolyte and conducted at a higher current density, hence the period of time required for the decrease of the micro-hardness of the deposits and attaining a permanent value is considerably reduced to within one week.¹ The fact was also supported by the XRD determination.⁵ Therefore, the micro-hardness measurements were performed on polished cross sections using a Vickers micro-hardness tester with a 25 g load after one week. The crystallographic structure of the deposits was examined with XRD. DSC was conducted at a rate of 10°C/min. According to our previous work,³ cyclic voltammetric stripping (CVS) experiments of these copper electrolytes were performed. The surface morphology and grain size of the copper deposits was examined using SEM.

Results and Discussion

1. PEG and thiourea derivative additives

According to our previous literature on copper electroplating that PEG with greater surface activity will have a lower Ar/As value in the CVS determination.² A further study into the literature shows that the surface activity of the PEG-containing electrolyte increases with increasing the MW of the PEG. Accordingly, as shown in Table 1, the MW of PEG is also a factor for the determination of the Ar/As values. The Ar/As values decrease with increasing the MW of the PEG; therefore, the suppression of cathodic current increases with increasing the MW of PEG. Similar observation is obtained for the thiourea derivative additives in copper baths. Owing to the cathodic current of copper deposition decreases with the increase of the MW of thiourea derivatives, as shown in Table 2, the Ar/As value of the CVS results also decreases with increasing the MW of these thiourea derived additives.

According to the results of Tables 1 and 2, PEG and thiourea derivatives with greater MW have greater adsorption on the cathode. This decreases the effective plated area, causing a decrease in the double-layer capacitance during the electrolysis. Consequently, the physico-mechanical properties of the copper deposits were affected by the MW of the additives. However, the surface activity properties of the additive-containing electrolytes are poor, only small change of the surface activity was observed by the change of the additives. On the other hand, the MW change of the additives is quite obvious, hence the correlation between the MW of additive and the mechanical property of the deposits is clearer than that of surface activity. As a result, a further study on the MW effect of additives on the prediction of the physico-mechanical properties of the copper deposits is conducted.

Table 1					
Relative Rate Parameter Ar/As,					
vs. MW of PEG					
	Added				
	Average	Concentration			
Additives	MW	ppm	Ar/As		
PEG 400	400	32	0.88		
		42	0.82		
		52	0.77		
PEG 1000	1000	32	0.80		
		42	0.77		
		52	0.73		
PEG 4000	4000	32	0.40		
		42	0.37		
		52	0.37		
PEG 6000	6000	32	0.10		
		42	0.07		
		52	0.06		

2. CMC additives

Similar to other organic additives in acid copper sulfate baths, as shown in Fig. 1, copper deposits obtained from the CMC-containing bath are characterized by small grains with better uniformity, causing a higher limiting current density than that of the base electrolyte (without organic additives). Therefore, CMC is a practical additive in the copper electrolyte. As predicted by the results of MW effect of PEG and thiourea derivatives, the Ar/As values were also affected by the MW of CMC in the copper electrolyte. As shown in Table 3, the Ar/As values decreases with the increase of MW of CMC. This is another clear evidence of the stronger blocking effect of a greater MW of additives than that of low MW. Therefore, CMC with a greater MW exerts a stronger interfacial inhibition, causing a greater change of the double layer near the cathode surface. Accordingly, the nucleation, growth, and the physico-mechanical properties of the copper deposits should be strongly influenced by the MW effect of CMC.

Table 2 Relative Rate Parameter Ar/As,					
Added					
	Average	Concentration			
Additives	MW	ppm	Ar/As		
Thiourea	76.1	2	1.17		
		4	0.89		
		6	0.72		
Ethylthiourea	104.1	2	0.81		
		4	0.69		
		6	0.39		
p-Tolylthiourea	167.2	2	0.11		
		4	0.09		
		6	0.07		

The MW effect of CMC on the copper deposits was supported by their diffraction patterns of XRD. Copper plated in the presence of CMC exhibited the strongest reflection was the [110] orientation. As shown in Fig. 2, owing to the MW effect on the deposit structure, both of the degrees of [111] and [200] orientations are higher for the CMC9-containing bath. On the other hand, the addition of greater MW of CMC results in high [110] orientation. Accordingly, the MW of CMC has a relevant influence on the micro-structure and then the physico-mechanical properties of the copper deposits.

Table 3 Relative Pate Parameter Ar/As					
Kela		of CMC			
	VS. IVI VV				
		Added			
	Average	Concentration			
Additives	MW	ppm	Ar/As		
CMC9	90,000	1	0.98		
		2	0.93		
		4	0.79		
CMC25	250,000	1	0.90		
		2	0.78		
		4	0.73		
CMC70	700,000	1	0.87		
		2	0.72		
		4	0.65		



Fig. 1 - Typical surface morphology of copper deposits obtained at 2 A/dm^2 from (a) base electrolyte, (b) electrolyte containing 1 ppm of CMC9.

The MW effect of CMC was also studied by the peak intensity



Fig. 2 – X-ray diffraction patterns of the copper deposits obtained at 8.5 A/ dm^2 when the baths containing (a) 1 ppm CMC9, (b) 3 ppm CMC9, (c) 1 ppm CMC70 and (d) 3 ppm CMC70.

ratio of XRD. The [111]:[200] peak intensity ratios for copper plated in the presence of CMC9 were found to be 100:69.6 and 100:92.0, Figs. 2a and 2b. Whereas the corresponding copper plated in the presence of CMC70-containing baths yields the peak intensity ratios of 100:35.7 and 100:91.1, Figs. 2c and 2d. It is therefore clear that the copper plated in the presence of CMC70 exhibits a predominantly [111] orientation.⁶ The [111] orientation is the close-packed plane (e.g., highest atomic density plane), resulted in the deposits obtained from the CMC70containing bath should have greater mechanical properties than those of CMC9-containing baths. Accordingly, as shown in Table 4, the micro-hardness of the deposits obtained from the CMC-containing baths increases with increasing the MW of CMC. The deposits obtained from the electrolyte containing CMC70 had greater micro-hardness than that of CMC9. As shown in Table 4, the micro-hardness of the deposits is affected by the current density and the CMC concentration in the electrolyte. Although Stoychev¹ previously indicated that the microhardness of the deposits increases with the amount of codeposited carbon of copper deposits, the micro-hardness was not increased by the concentration of CMC. The apparent grain size of the deposits could be used to explain the phenomenon. As shown in Fig. 3, the grain size of the copper deposits obtained from the CMC-containing baths does not decrease with increasing the concentration of CMC. Owing to a small grain size will have greater hardness, causing the deposits obtained from the bath containing around 2 to 3 ppm of CMC have a greater hardness.



Fig. 3 - Typical SEM photograph of grain sizes of copper deposits obtained at 8.5 A/dm² when the baths containing (a) 1 ppm CMC9, (b) 3 ppm CMC9, and (c) 5 ppm CMC9.

The MW of the CMC added in the copper bath affects not only the mechanical properties but also the thermal stability. The DSC curves of the copper deposits were investigated to explain the thermal phenomenon. DSC shows heat flow at the phase transformation temperature of the deposits.⁷ As shown in Fig. 4, the exothermic peak of the copper plated in the presence of CMC70 indicates that the phase transformation temperature is greater than 250°C, whereas the corresponding copper plated in the presence of CMC9 yields a phase transfer temperature lower than 250°C. Therefore, the results of DSC measurement indicate that the thermal stability of the copper deposits increases with the increase of the MW of CMC in the copper baths.

Conclusions

Owing to the different molecular weight of organic additives, different Ar/As ratio was determined in the acid copper electrolyte, causing the copper plated has different physico-mechanical properties. According to the results of electrochemical analysis, XRD, and DSC, CMC with greater molecular weight will make the plated copper with greater micro-hardness and thermal-stability properties.



Fig. 4 – DSC curves of the copper deposits obtained at 8.5 A/dm² when the baths containing (a) 3 ppm CMC9, (b) 1 ppm CMC9, (c) 3 ppm CMC70, and (d) 1 ppm CMC70.

References

- 1. D. Stoychev, Trans IMF, 76(1), 26 (1998).
- 2. H.M. Wu et al., Chemistry (The Chinese Chemical Society), 48(3), 233 (1990)
- 3. H.M. Wu et al., Plat. & Surf. Fin., 79, 66 (September 1992).
- 4. D. Stoychev, Trans IMF, 76(2), 73 (1998).
- 5. D.S. Stoychev et al., J. Appl. Electrochem., 15, 879 (1985).
- 6. E.D. Eliadis and R.C. Alkire, J. Electrochem. Soc., 145(4), 1218 (1998).
- 7. N.M. Martyak et al., Metal Finish., 92, 111 (June 1994).

Table 4						
Micro-hardness of the Deposits Obtained from the CMC-Containing Electrolyte						
	Concentration of CMC, ppm					
Additive	Current Density, A/dm ²	0	1	2	3	4
CMC9	2	63	85	88	80	78
	3	72	88	88	93	86
	8.5	88	96	102	99	96
CMC7	2	63	91	93	93	90
	3	74	104	110	112	100
	8.5	90	112	112	112	106