Effect of Additives on Morphology of Copper Deposits During Pulse Plating

Nisit Tantavichet and Mark D. Pritzker
Department of Chemical Engineering,
University of Waterloo,
Waterloo, Ontario, Canada N2L 3G1

A major goal of electrodeposition is to obtain suitable deposit properties for different applications (e.g., compactness, uniformity, smoothness and grain orientation). Two ways to accomplish this are the addition of additives and the use of pulse plating instead of DC plating. Generally, additives affect electrocrystallization through such mechanisms as inhibition of adatom diffusion by blocking active sites or enhancement of the nucleation process [1,2]. Pulse plating can improve mass transport of depositing species and enhance crystal nucleation through higher instantaneous current densities [3,4]. Numerous studies have been devoted to the use of additives or pulse plating, but relatively few have dealt with the combination of the two.

This study is concerned with the galvanostatic pulse current (PC) plating of copper onto a rotating disc electrode in a 0.1 M $CuSO_4$-1M H_2SO_4 bath containing various additives (e.g., thiourea, polyethylene glycol (PEG) and Cl^-). Deposits so formed are compared to those produced without additives and/or via DC plating. An average current density of 4 A dm^{-2} was applied for 12 minutes in all cases to obtain a deposit thickness of 10 µm. The electrode responses during electrodeposition were monitored with a digital oscilloscope. Images of the deposits were obtained using SEM, while their specular reflectances were measured with a scatterometer (1300 nm source).

Electrodeposit reflectances obtained under various conditions are shown in Table 1. As reference, an uncoated, mechanically polished (0.5 µm Al_2O_3) copper disc has a reflectance of 92%. In additive-free solutions, PC plating improves deposit reflectivity over that achieved via DC plating. Moreover, reflectance increases as the duty cycle decreases. A reduction in duty cycle moves electrolysis further away from DC conditions, requiring higher pulse amplitudes to maintain the time-averaged current fixed. This leads to a more negative electrode potential during the cathodic portion of the cycle, a higher crystal nucleation rate and finer grain size.

The addition of 300 µM PEG alone has little effect on deposit reflectance during DC plating and PC plating at every duty cycle studied. The corresponding SEM images and electrode responses show very little change in deposit morphology and electrode potentials from those obtained in the absence of additives. While PEG alone has little effect, the same cannot be said for the influence of Cl^- ions. In the presence of 10 ppm Cl^- along with PEG (Table 1) or in the absence of any other additives, very dull deposits with large grains are obtained regardless of the mode of electrolysis. The electrode responses show substantial shifts to more negative potential from those obtained in additive-free electrolyte.

As expected, thiourea has a positive effect on surface brightness under most conditions. As shown in Table 1, very bright deposits with reflectances above 80% are obtained when 20 µM thiourea alone is present (Fig. 1a). In these solutions, PC plating confers no advantages to deposit quality over that achievable via DC plating.

The combination of chloride ion and thiourea leads to very interesting results. Under these conditions, the mode of electrolysis has a significant effect. DC plating leads to unpatterned rough deposits. However, when current pulses are applied, differences in roughness on a macro-scale and micro-scale occur. Although a very bright surface is produced on a micro scale, a spiral pattern covering most of the electrode surface and mirroring the rotation of the electrode (Fig. 2) is produced. An increase in Cl^- concentration to 35.6 ppm during PC plating leads to the best overall results of this study, yielding smooth, uniform and very bright deposits (92%) without the spiral patterns and any macro-roughness observed at 10 ppm Cl^- (Fig. 1b). Similar results are achieved regardless of duty cycle at a frequency of 50 Hz. In contrast, an increase in Cl^- concentration from 10 ppm to 35.6 ppm at a 20 µM thiourea during DC plating does not affect deposit quality on a micro-scale, which remains rough, but leads to the appearance of a large rough, spiral pattern.

Clearly, a complex interaction occurs between the mode of electrolysis, electrolytic composition and hydrodynamics. Further details and experimental results will be presented in this paper.

References

[1] G. Fabricius, K. Kontturi and G. Sundholm, *Electrochimica Acta*, **39**, 2353 (1994).
[2] W. U. Schmidt, R. Alkire and A. A. Gewirth, *J Electrochem. Soc.*, **143**, 3122 (1996).
[3] P. Cl. Puippe and F. Leaman (Editors), Theory and Practice of Pulse Plating, AESF (1986).
[4] G. Holmbom and B. E. Jacobson, *J Electrochem. Soc.*, **135**, 2720 (1988).

Table 1 *Deposit reflectances*

Plating Mode	no additive	300 µM PEG	300 µM PEG & 10 ppm HCl	20 µM Thiourea
DC	38%	40%	1.7%	82%
PC (80%)	41%	48%	4.4%	82%
PC (50%)	62%	60%	3.8%	84%
PC (20%)	72%	67%	2.2%	58%

Note: 1. All pulse current plating is carried out at 50 Hz.
2. Rotational speed of the disc electrode is 500 rpm.

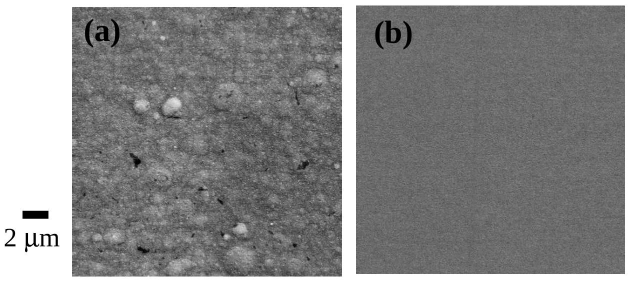

Fig. 1 SEM images of coating produced by PC plating at 50 Hz and 80% duty cycle in (a) 20 µM thiourea (b) 20 µM thiourea + 35.6 ppm Cl^-

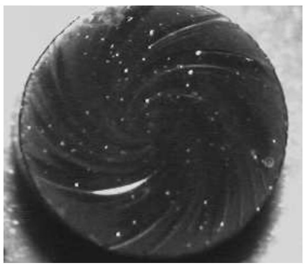

Fig. 2 Optical microscope image of coating produced by PC plating at 50 Hz and 80% duty cycle in 20 µM thiourea + 10 ppm Cl^-