

Comparative Study of Organic Acids as Complexing Agents in Copper Electrodeposition

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Organic acids are frequently employed as complexing agents in electroplating baths for production of thin metallic films in many application areas, and a clearer understanding of their role in the deposition mechanism should be of considerable use in the development of reliable and efficient plating technologies in the future. In this connection, plating baths for copper deposition have been the focus of much attention in recent years, in large part due to the considerable interest in copper as an interconnect material for integrated circuits. Research reported previously [1] on the role of citrate, an acid-alcohol, in aqueous plating baths for copper indicated that coordination chemistry involving deprotonation of the citrate alcohol group in the presence of cupric ions in solution plays a major role in the deposition mechanism.

A striking feature of the citrate system is the extremely strong dependence of the copper deposition potential on solution pH. Copper deposition at moderate current densities from copper plating baths containing excess citrate can exhibit shifts of more than 900 mV between pH 3 and pH 7. Comparison of measured polarization curves, combined with titration experiments and calculations of the distribution of complexed species in solution, suggests strongly that the shift in deposition potential is directly related to deprotonation of the alcohol group.

On the basis of these observations, a two-step deposition mechanism has been proposed, involving an adsorbed blocking intermediate directly related to the deprotonated complexes, in competition at available surface sites with direct discharge of protonated complexes. The kinetic mechanism, when combined with the distribution of complexed species determined from the model for copper-citrate solutions proposed by Daniele and De Robertis [2], is capable of representing successfully the behavior observed for copper deposition from complexing baths containing excess citrate and has demonstrated predictive capabilities of particular interest for the optimization of plating processes.

The goal of the present work is to expand upon the previous study, by comparing the behavior of citrate baths to other complexing baths containing similar organic acids. In this regard, particular attention is given to baths derived from malic acid, an acid-alcohol with a structure similar to that of citric acid.

Experimental results from baths containing excess malate, and similar results for citramalate, tartrate, lactate and glycolate, suggest that the hypothesis of a specific role for the alcohol group is indeed justified.

To confirm this hypothesis further, experimental comparisons have been extended to baths derived from tricarballic acid, an organic acid with a structure practically identical to that of citric acid, but without the alcohol group. As expected from the proposed mechanism, no significant effect of solution pH on the copper deposition potential is observed for tricarballic baths, a result that provides additional strong support to the hypothesis.

Based on the experimental comparisons, the kinetic mechanism for copper deposition from plating baths derived from citric acid has been extended to a more general family of organic acids. The essential features of the more general mechanism are presented and discussed, and possible applications of the approach for the development of innovative plating technologies are suggested.

[1] Ch. Henninot, C. Vallières, S. Rode and M. Matlosz, *Electrochemical Society Proceedings Volume*, **99-34**, 333-339 (1999).

[2] P. G. Daniele and A. De Robertis, *Transition Metal Chemistry*, **13**, 87 (1988).

