

## Application of saccharose as copper(II) ligand for electroless copper plating solutions

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**Abstract**—Saccharose, forming sufficiently stable complexes with copper(II) ions in alkaline solutions, was found to be a suitable ligand for copper(II) chelating in alkaline (pH > 12) electroless copper deposition solutions. Reduction of copper(II)–saccharose complexes by hydrated formaldehyde was investigated and the copper deposits formed were characterized. The thickness of the compact copper coatings obtained under optimal operating conditions in 1 h reaches ca. 2 μm at ambient temperature. The plating solutions were stable and no signs of Cu(II) reduction in the bulk solution were observed. Results were compared with those systems operating with other copper(II) ligands.

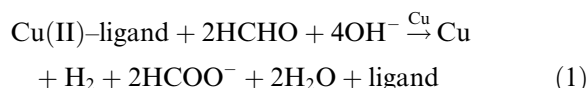
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**Keywords:** Saccharose; Ligand; Copper(II); Electroless copper deposition; Copper coatings; Surface roughness

### 1. Introduction

Electroless copper plating solutions are widely used in electronics for deposition of metallic copper layers on semiconductors or dielectrics (silicon wafers, resins, etc.).<sup>1,2</sup> The electroless deposition method uses a catalytic redox reaction between metal ions and dissolved reduction agent, and the main advantages of this technique is a possibility to plate nonconductive surfaces and to obtain metal coatings of the uniform thickness all over the plated object.

The overall process of electroless copper deposition is described by the following equation:



In general, electroless metal deposition processes are recognized now to be electrochemical by nature and are supposed to result from the coupling of two partial elec-

trochemical reactions—the cathodic reduction of metal ions and the anodic oxidation of the reducing agent. Electroless copper deposition process consists of anodic formaldehyde oxidation and cathodic Cu(II) reduction occurring simultaneously on the same copper surface; the electrons that appear in anodic oxidation of formaldehyde are transferred through the metallic copper to Cu(II) ions, and the autocatalytic deposition of Cu takes place.

Copper(II) ligands, along with hydrated formaldehyde as the reducing agent and a copper(II) salt as copper(II) ions source, are important components of autocatalytic copper deposition systems. Since these systems operate in alkaline milieu, the ligands used must meet several important requirements: these compounds must form copper(II) complexes that are stable enough to prevent precipitation of copper(II) hydroxide, and they should not react with formaldehyde nor retard the catalytic copper(II) reduction reaction. Ethylenediaminetetraacetic acid (EDTA) is currently the most widely used ligand in electroless copper plating technique due to its perfect chelating properties. However, there are attempts to replace EDTA, because it creates environmental hazards.

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Xylitol, D-mannitol and D-sorbitol were proposed recently as environmentally friendly alternate copper(II) ligands for electroless copper plating solutions.<sup>3</sup> The alditols mentioned showed good chelating properties for copper(II) ions in alkaline media (pH > 11.5).<sup>4</sup> Electroless copper plating solutions containing the chelators xylitol, D-mannitol and D-sorbitol are stable and, under optimal conditions, copper coatings up to 3  $\mu\text{m}$  thick can be obtained in 1 h at ambient temperatures.<sup>3</sup>

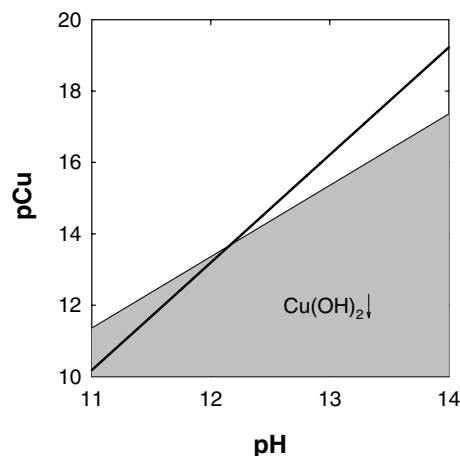
The ability of polyols to chelate Cu(II) ions in alkaline solutions has been known since the 19th century, but quantitative data on the composition and stability of the complexes formed are sparse. Data on the interactions of saccharose (Sa) with Cu(II) ions in alkaline medium were published in the late 20th century.<sup>5,6</sup> It was found that the chelating ability of saccharose depends on solution pH and the concentrations of Cu(II) and saccharose. The pH-dependence is related to deprotonation of saccharose in alkaline solutions ( $\text{p}K_{\text{a}} = 12.43$ ) and formation of the  $\text{Sa}^-$  anion, which is the main chelator in the systems investigated. Generally, formation of soluble Cu(II)–saccharose compounds is observed at pH values > 10. This pH limit depends also on Cu(II) concentration and the degree of excess of saccharose. Three mononuclear copper(II)–hydroxy complexes were documented under conditions of saccharose excess:  $\text{CuSa}(\text{OH})_2^-$  ( $\log \beta = 17.6$ ),  $\text{CuSa}(\text{OH})_3^{2-}$  ( $\log \beta = 19.4$ ) and  $\text{CuSa}_2(\text{OH})_2^{2-}$  ( $\log \beta = 19.6$ ).<sup>5,6</sup>

Since composition and stability of Cu(II) complexes with xylitol<sup>4</sup> are similar to those of Cu(II)–saccharose, the aim of the study presented herein was to evaluate the electroless copper deposition process in solutions containing saccharose as the Cu(II) ligand.

## 2. Results and discussion

### 2.1. Equilibria in alkaline copper(II)–saccharose solutions

The values of stability constants of Cu(II)–saccharose complexes lead to a prediction that at the Cu(II) concentration (0.05 M) commonly used in electroless copper plating solutions, saccharose should be able to adequately chelate Cu(II) ions under conditions of saccharose excess. Calculations indicate that saccharose is able to chelate 0.05 M Cu(II) sufficiently to prevent  $\text{Cu}(\text{OH})_2$  precipitation at pH values > 12. That is, calculated pCu (i.e., negative logarithm of uncomplexed Cu(II) ions) values are higher than those necessary to prevent precipitation of copper(II) hydroxide, and  $\text{Cu}(\text{OH})_2(\text{s})$  should not form (Fig. 1). Experiments confirmed these predictions—no  $\text{Cu}(\text{OH})_2(\text{s})$  precipitate was observed at pH values > 12 and solutions became dark blue, whereas at lower pH values formation of  $\text{Cu}(\text{OH})_2(\text{s})$  is clearly visible.

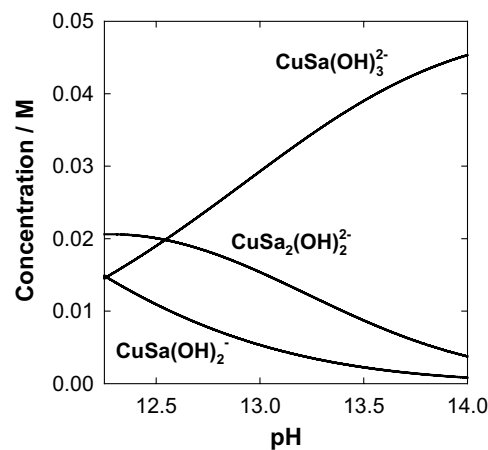


**Figure 1.** Relationships of pH to pCu in saccharose containing solutions. Solution composition (M):  $[\text{Cu}(\text{II})]_0 = 0.05$ ;  $[\text{Sa}]_0 = 0.10$ . Filled areas represent regions of  $\text{Cu}(\text{OH})_2$  precipitate formation.

Calculations of the distribution of Cu(II) among the complexes with saccharose show that a mixture of Cu(II)–saccharose complexes is formed in the solution (Fig. 2). No predominate species is observed in pH region from 12.25 to 13, whereas at pH 13, ca. 50% of Cu(II) is in the form of the  $\text{CuSa}(\text{OH})_3^{2-}$  complex, which clearly predominate at higher pH values.

### 2.2. Electroless copper deposition from solutions containing saccharose as Cu(II) ion ligand

In solutions with an excess of saccharose (Cu(II)/saccharose molar ratio 1:2), autocatalytic reduction of Cu(II) by formaldehyde starts at pH (Fig. 3). The plating rate near the lower pH limit (pH 12.25) is ca.  $0.5 \mu\text{m h}^{-1}$ . With further increase in solution pH, the plating rate rises sharply reaching maximum values at a pH near 12.75, and then decreases as the pH is further elevated.



**Figure 2.** Distribution of Cu(II) among the complexes in solution containing (M):  $[\text{Cu}(\text{II})]_0 = 0.05$ ;  $[\text{Sa}]_0 = 0.10$ .

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