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# Role of additives in an eco-friendly electroless copper deposition bath

**Jayalakshmi Suseela[a]*, Venkatesh Perumal[a] and Balaramesh Palanivelu[b]**

[a]Department of Chemistry, Pachaiyappa's College, Chennai-600 030, India

*E-mail:* jlakshmi2007@gmail.com

[b]Department of Chemistry, RMK Engineering College, Chennai-601 206, India

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This article reports the effect of additives in an eco-friendly electroless copper deposition bath containing glycerol as the complexing agent and dimethylamineborane (DMAB) as the reducing agent. The copper methanesulphonate bath was studied by adding stabilizers such as tolytriazole (TTA) and cytosine (CYS) with potassium hydroxide as the pH adjuster. The electroless bath was optimized by the addition of 1 ppm concentration of stabilizers at 11.50±0.25 pH. The effect of stabilizers on plating bath were studied and reported. Surface morphologies of the electroless copper coated epoxy substrates were investigated using Scanning Electron Microscope (SEM) and surface roughness by Atomic Force Microscopic (AFM) analysis. Crystallite size and specific surface area of copper thin film were observed by X-ray diffraction (XRD). Electrochemical characteristics were studied by cyclic voltammetry while the CYS does not have much effect.

Keywords: Glycerol, dimethylamineborane, tolytriazole, cytosine, crystallite size.

## Introduction

Electroless copper plating is widely used for the fabrication of printed circuit boards and other electronic devices. There is renewed interest in copper deposition for ultra-large scale integrated circuits (ULSI) because of the higher conductivity of copper versus aluminum[1–3]. The effects of eco-friendly polyhydroxylic compound, glycerol as complexing agent on the electrochemical reduction of cupric ions and the oxidation of DMAB on epoxy substrates have been investigated. TTA and CYS are used as stabilizers. TTA has superior qualities and it is used as anti-corrosive additive in cooling and hydraulic fluids, antifreeze formulation, aircraft deicer and anti-icer fluid (ADAF) and dishwasher detergents for silver protection. TTA is found to enhance the deposition while the CYS comparatively has no much effect than the glycerol plain bath.

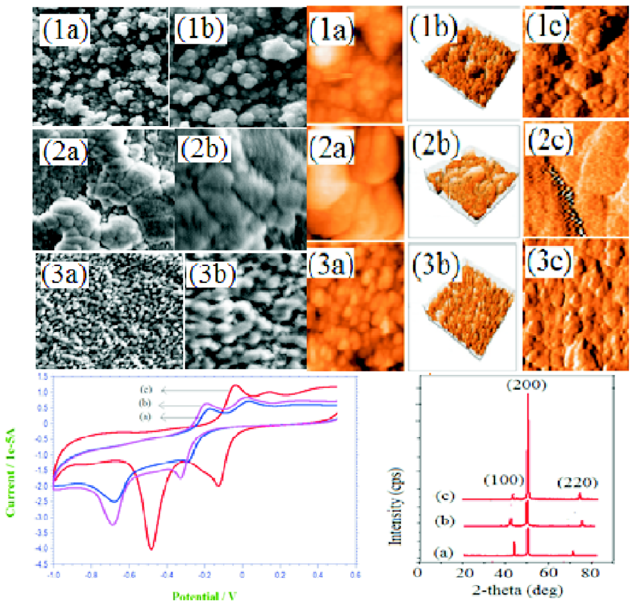


**Fig. 1.** AFM, SEM, CV and XRD studies of copper methanesulphonate glycerol plain bath with TTA and CYS stabilizers.

## Results and discussion

Cyclic voltammetry was carried out to study the electrochemical properties of electroless copper solution and the role of the stabilizers[6]. The result shows the accelerating nature of both TTA and CYS, while the former is found to enhance the deposition and the latter has no much effect compared to the glycerol plain bath.

**Table 1.** Bath composition of copper methanesulphonate glycerol plain bath with stabilizers

| Bath contents | Plain bath | Stabilizers used bath |
|---|---|---|
| CuMS (II) ion contacting salt (g/L) | 3 | 3 |
| Glycerol (ml/L) | 20 | 20 |
| Dimethylamine borane (g/L) | 5 | 5 |
| KOH (pH ) | 11.50±0.25 | 11.50±0.25 |
| Temperature (°C) | 28±2 | 28±2 |
| Stabilizers (TTA and CYS) (ppm) | 0 | 1 |

The surface morphology of copper deposits was studied by scanning electron microscopy (SEM) analysis at magnification of ×1000 and ×5000 for the specimen used in plain bath and additive baths. The study shows that TTA results in smooth shiny honeycomb shaped deposits and modifies the physical properties of the copper deposits compared to the CYS (fine grains) and glycerol plain bath (coarse grains).

Bright copper deposits seen in atomic force microscopy (AFM) indicate better mechanical and physical properties. Roughness values are inversely propositional to smooth deposition.

**Table 2.** Physical and surface morphologies of glycerol plain bath with stabilizers (1 ppm) on electroless copper bath

| Surface morphology | Glycerol plain bath | Stabilizers used glycerol baths | |
|---|---|---|---|
| | | CYS | TTA |
| Crystallite size (nm) | 121 | 117 | 111 |
| Deposition rate (μm/h) | 3.18 | 3.23 | 3.34 |
| Anodic peak potential, Epa-1 (mV) | –0.2695 | –0.2549 | –0.1666 |
| Roughness value (nm) | 23.411 | 22.930 | 22.485 |
| Thickness (μm) | 190.8 | 193.8 | 200.4 |
| Specific surface area ($m^2$/g) | 5.534 | 5.723 | 6.033 |

Copper methanesulphonate bath results in large quantities of copper ions, because of high conductivity and solubility leading to (200) plane[7,8]. The crystallite size the copper deposits can be estimated by using Debye Scherrer's equation[9,10].

$$D = K\lambda/\beta \cos\theta$$

Specific surface area of the copper deposits is determined by the

$$s = \frac{6\times10^3}{\rho d}$$

## Conclusions

Copper methanesulphonate bath with eco-friendly natural polyhydroxylic compound, glycerol used as complexing agent was studied with two different stabilizers. The complexing agent were found to form stable complexes with copper ions in the alkaline medium. Physical and electrochemical experimental techniques were used to characterize the deposited copper.

Electroless methanesulphonate baths with TTA produced brightest honeycomb shaped copper deposits with better physical and electrochemical properties while CYS showed fine grains shape and the glycerol plain bath with coarse grains shape in the copper deposition.

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