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# Electroless Copper Nano Thin Film Deposition Using Ecofriendly Natural Polyhydroxylic Compound

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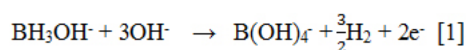
***Abstract***
*Copper electroless plating using polyhydroxylic alcohol was studied electrochemically using Dimethylamineborane(DMAB) as reducing agent. Copper methanesulphonate bath was used with Glycerol as the complexing agent and Potassium hydroxide as pH adjuster. The electroless bath was optimized by addition of 1 ppm concentration of stabilizers at 11.50 ± 0.25 pH. Tolytriazole(TTA) and Cytosine(CYS) are used as stabilizers and their effects 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 (CV). The physical parameters of the deposition shows that TTA influenced the copper coating while the CYS does not show much effect.*

**Keywords:** Glycerol, Dimethylamineborane, Tolytriazole, Cytosine, Crystallite size

## Introduction

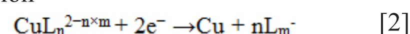
Electroless copper plating is widely used for the fabrication of printed circuit boards and other electronic devices. There is renewed interest in copper deposition for ultra-large scale integrated circuits (ULSI) because of the higher conductivity of copper versus aluminum [1-4]. Electroless copper plating is well suited for uniform copper deposition on a variety of substrates. The deposition rate and deposit properties of electroless copper plating depend on the copper complexing agent, reducing agent, bath temperature and pH [5]. In addition, additives such as stabilizers, accelerators and brighteners are used [6]. The use of a complexing agent in the bath is essential because it prevents precipitation of Cu(OH)2 under alkaline solution conditions. The effects of eco-friendly polyhydroxylic compound Glycerol as complexing agent on the electrochemical reduction of cupric ions and the oxidation of Dimethylamineborane(DMAB) on epoxy substates have been investigated. Oxidation of the reducing agent employed involves the formation of hydrogen (H') ions. Consequently, the pH of the plating solution changes during plating and thus affects the rate of deposition and the properties of the deposit. Therefore, buffers (KOH) are added to stabilize the pH of the solution.

Electroless copper plating with DMAB as reduction agent can be described by the following two half-cell reactions.
Anodic reaction



$$BH_3OH^- + 3OH^- \rightarrow B(OH)_4^- + \frac{3}{2}H_2 + 2e^- \quad [1]$$

Cathodic reaction



$$CuL_n^{2-n\times m} + 2e^- \rightarrow Cu + nL_m^- \quad [2]$$

Where L represents the complexing agent and m denotes the charge of the complexing agent. In this work, we have studied the influence of stabilizers on an ecofriendly copper methanesulphonate bath with glycerol as the complexing agent. Tolytriazole and Cytosine are used as stabilizers [7,8]. 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 [9,10]. TTA is found to enhance the deposition while the CYS comparatively has no much effect in the plating rate.

## Material and methods

The electroless Cu deposition was performed on an epoxy sheet (2.0 x 2.0 x 0.1 cm) in a 100 ml beaker. The epoxy sheet was polished by grit paper, rinsed with distilled water. After rinsing the substrate was surface etched using a solution of KMnO4 and H2SO4 to remove any oxidized layer on the surface. In order to improve the deposition rate and adhesive properties of the Cu thin film, the surface was sensitized using SnCl2 solution (SnCl2 mixed with HCl) and activated using an HCl solution of PdCl2. Figure.1 and table.1 shows the multi-step process involved in electroless plating and the bath composition.

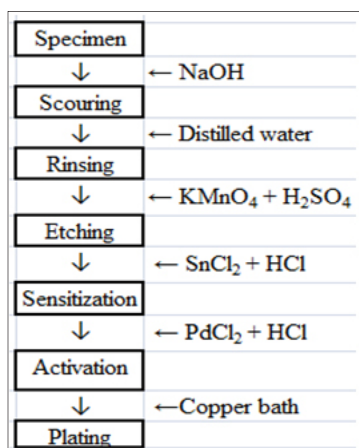



**Figure1**: Flow chart for electroless copper plating process.

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

| Bath contains | Plain bath | Stabilizers used bath |
|---|---|---|
| CuMS (II) ion contacting salt | 3 g/L | 3 g/L |
| Glycerol | 20 ml/L | 20 ml/L |
| Dimethylamineborane | 5 g/L | 5 g/L |
| KOH (*p*H ) | 11.50 ± 0.25 | 11.50± 0.25 |
| Temperature | 28 ± 2 ºC | 28 ± 2 ºC |
| Stabilizers (TTA &Cys) | 0 ppm | 1 ppm |

The rate of deposition (T) was calculated using the following relation

$$T = W \times 10^4 / dAt \quad [3]$$

Rate of the electroless copper deposit and thickness were calculated using the following equation

$$Rate\ of\ deposition\ (\mu m/h) = Thickness\ /\ Deposition\ time \quad [4]$$

$$Thickness(\mu m) = \frac{W \times 10^4 \times 60}{A \times D} \quad [5]$$

Where,
W = ($w_1$-$w_2$) = Weight of deposit (g)
$w_1$ = Weight after plating (g)
$w_2$ = Weight after stripping (g)
A = Total plated area of the substrate ($cm^3$)
D = Density of the copper (8.96 g/$cm^3$)

## Results and discussion

Methanesulphonate bath containing glycerol produced stable complexes with copper (II) ion in alkaline solutions. The optimum deposition rate was observed at pH 11.50 ± 0.25 beyond which the deposition slowed down. In the absence of stabilizers, the rate of plating was poor [11-13].The inhibiting or accelerating properties of the stabilizers were compared in terms of the deposition rate (μm/h) of the electroless plating plain bath. The effect of addition of small amount of stabilizers like TTA and CYS on the rate of deposition, physical and surface morphologies were studied.

**Table 2: Influence of various physical and surface morphologies of glycerol plain bath with stabilizers (1 ppm) on electroless copper bath**

| Surface morphologies | 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) | -0.2168 | -0.1999 | -0.1666 |
| Roughness value (nm) | 202 | 114 | 108 |
| Thickness (μm) | 190.8 | 193.8 | 200.4 |
| Specific surface area ($m^2$/g) | 5.534 | 5.723 | 6.033 |

## Electrochemical studies

Cyclic voltammetry was carried out to study the electrochemical properties of electroless copper solution and the role of the stabilizers [14]. The voltammograms were recorded at room temperature 28 ± 2 ˚C in 0.1 M Na2SO4 as supporting electrolyte and the concentration of copper solution and DMAB were 0.005 M. Micro-disk of standard type glassy carbon electrode was used as working electrode and the voltammograms were recorded in the range from -1.2 to +0.5 V at potential scanning rate 50 mVs-1.The 0.1M Na2SO4 supporting electrolyte solution was optimized by KOH solution at pH 11.50 ± 0.25 for glycerol baths. In Figure.2 and Table.2 it is seen that the inhibiting and enhancing properties of stabilizers are confirmed by the anodic peak current value, anodic peak potential value and peak appearance.

Based on CV studies, the inhibiting properties of the stabilizer result in low anodic peak potential value. The low energy oxidation process is enhanced by the stabilizers. The appearances of the sharp peaks indicate that the rate of oxidation is high. The high anodic peak current value also indicates that the stabilizer inhibits the deposition of copper. The low anodic peak current, high peak potential and broad peaks indicate the enhancing properties of the stabilizers. Glycerol bath with TTA shows higher Epa-1(-0.1666) value with CYS (-0.1999) and Glycerol plain bath with the least (-0.2168) value. The value 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.

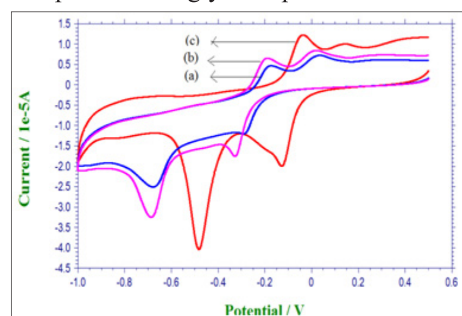



**Figure 2**: Cyclic voltammogram for electroless copper methanesulphonate glycerol bath (a) Glycerol plain bath, (b) CYS bath and (c) TTA bath.

## Scanning electron microscopy (SEM)

The two dimensional structure of deposited copper was studied by SEM analysis. The surface morphology of copper deposits

was studied by scanning electron microscopy (SEM) analysis at magnification of x 1000 and x 5000 for the specimen used in plain bath and additive baths. Figure.3. shows that regular and fine grained copper deposits were obtained when the additives were added to the glycerol bath. Addition of small volume of stabilizers not only stabilizes the bath and also changes the physical features such as colour, shape and crystallite size of the copper deposits. Many interesting shapes like flower, honey comb, rock, needle and pyramid etc. were observed. The study also shows that TTA results in smooth shiny honeycomb shaped depositsand modifies the physical properties of the copper deposits compared to the CYS(fine grains) and glycerolplain bath(coarse grains).

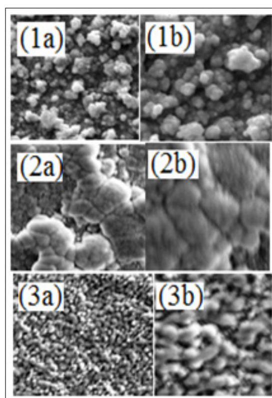



**Figure 3**: SEM images of copper deposits on (1) methanesulphonate glycerol plain bath with CYS (2) methanesulphonate glycerol plain bath (3) methanesulphonate glycerol plain bath with TTA; (a) magnification 1000 and (b) magnification 5000

## Atomic Force Microscope (AFM)

Bright copper deposits seen in atomic force microscopy (AFM) indicate better mechanical and physical properties. Roughness values are inversely propositional to smooth deposition. On addition of stabilizers, the deposits show changes in physical characteristics. Figure.4. and Table 2. Indicate the roughness values of the glycerol plain bath and bath with the two stabilizers. The glycerol plain bath shows the highest roughness value of 202nm with CYS bath of 114nm and the TTA bath showed the least value of 108nm.

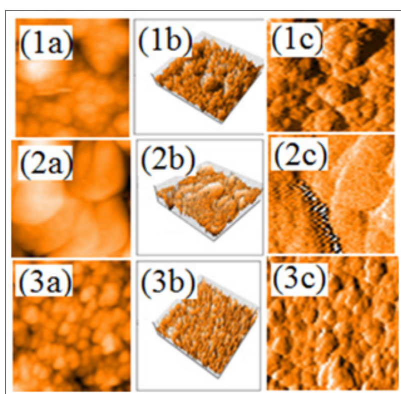



Figure 4: AFM images of (1) methanesulphonate glycerol plain bath with cytosine (2) copper methanesulphonate glycerol plain bath (3) methanesulphonate glycerol plain bath with tolytriazole; (a) topography of copper deposits (b) 3-D image and (c) surface area

## X-ray Diffraction (XRD)

Copper methanesulphonate bath results in large quantities of copper ions, because of high conductivity and solubility leading to (200) plane.Fig.5.shows the results of structural properties of the plain bath and the bath with stabilizers. The crystallite size of the copper deposits can be estimated by using Debye Scherrer's equation [15-18]. $D = K \lambda / \beta \cos\theta$

where K is the Scherrer constant, 'λ' is the wavelength of light used for the diffraction, 'β' is the 'Full Width at Half Maximum' of the sharp peaks and 'θ' is the angle measured [19,20]. The Scherrer constant (K) in the above formula accounts for the shape of the particle and is generally taken to have the value 0.89.

Specific surface area of the copper deposits is determined by the

$$S = \frac{6 \times 10^3}{\rho d} \qquad [6]$$

Where ρ is the crystallite size (nm) and d is the theoretical density of copper (8.96 g/cm3). Crystallite sizes are proportional to the inhibiting efficiency.

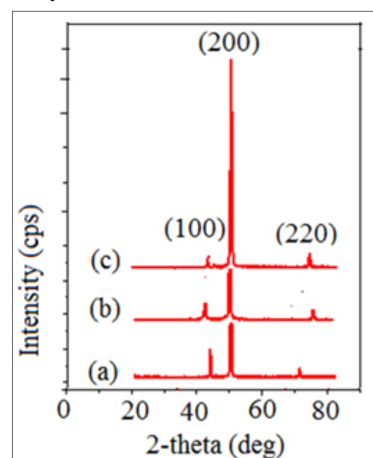



**Figure 5**: XRD pattern of copper deposits on methanesulphonate glycerol plain bath with stabilizers (1 ppm); (a) Glycerol plain bath (b) CYS (c) TTA.

## Conclusion

Copper methanesulphonate bath with ecofriendly natural polyhydroxylic compound Glycerol used as complexing agent was studied with two different stabilizers. KOH was used as pH adjuster to increase the solubility of the by-products during electroless copper deposition. The effects of pH, temperature and concentrations of reactants and additives on the anodic oxidation of DMAB and the cathodic reduction of copper ion were investigated. 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. The accelerating and inhibiting effects were determined by comparing the physical and electrochemical results of stabilizer containing baths with plain bath. Electroless methanesulphonate baths with tolytriazole produced brightest honeycomb shaped copper deposits with better physical and electrochemical properties while cytosine showed fine grains shape and the glycerol plain bath with coarse grains shape in the copper deposition.

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