

## Effects of environmental safe biodegradable compounds on ecofriendly electroless copper deposition

P. BalaRamesh<sup>1,\*</sup>, P. Venkatesh<sup>2</sup> and A. Sampath<sup>2</sup>

<sup>1</sup>Assistant Professor, Department of Chemistry, RMK Engineering College, Chennai, Tamilnadu, India.

<sup>2</sup>Associate Professor, Department of Chemistry, Pachaiyappa's College, Chennai, Tamil nadu, India.

Corresponding Author: E.Mail: balarameshp@gmail.com

### ABSTRACT

We have analyzed the effect of natural polyols on electroless deposition of copper from a bath that used ecofriendly complexing agents. Formaldehyde was used as reducing agent and KOH was used as pH adjustor to optimize the electroless plating bath. The deposition in saccharose and xylitol baths started at pH above 12. The novel feature of this work was the use of biodegradable glycine and methanesulphonic acid (MSA) as the stabilizer and bath liquid respectively. Glycine and MSA were found to influence the deposition by forming stable complexes with copper ions in alkaline solution, resulting in low enough concentration of free copper to prevent the precipitation of cupric hydroxide. Moreover, xylitol bath produced copper deposits that were finer and more compact than the saccharose baths. The surface morphology and texture of electroless copper deposits on the substrate were investigated using AFM, XRD analysis and the electrochemical characteristics of the ecofriendly electroless copper bath were determined by CV and Tafel studies.

**Keywords:** Crystallite size, formaldehyde, glycine, methanesulphonic acid, polyols.

### INTRODUCTION

There has been considerable research in recent years in developing and improving the self-initiating, autocatalytic process of electroless plating of metals, notably copper (Sullivan E.J.O., 2002) Electroless copper plating is used in many applications such as in the fabrication of decorative articles, semiconductors, integrated circuits and through-hole plating in printed circuit boards (Okinaka Y.,1994, Huang Q.,2000). Emerging applications of this technique lie in areas of electromagnetic interference shielding materials, ceramic or polymeric nanoparticles, aerospace, biomedical, automotive fields and energy conversion (Khaled K.F., 2009, Ling G.P., 2005, Yagi S., 2008). During electroless plating, a chemical reducing agent, rather than external electric current, provides electrons necessary to produce metallic deposits on a suitable substrate. Thus, this process is entirely chemical, thus the name 'chemical plating'. A chelating agent is usually used during electroless plating. Ethylenediaminetetraacidic acid (EDTA) is one of the most widely used chelating agent for electroless plating because it has excellent chelating properties over wide pH range and is stable up to 70 °C (Salkauskas M.,1985, Vaskelis A.,1986, Vaskellis A., 1991, Mallory G.O.,1990). However, the use of this chemical raises serious environmental concerns; EDTA forms stable heavy metal complexes, increases the total nitrogen content in waste water, and is only weakly biodegradable, which makes waste water treatment difficult (Lukes R.M.,1964, Schoenberg L.N., 1971). Alternate chelating agents are being sought to overcome the limitations of EDTA. Natural polyhydroxylic compounds such as saccharose and xylitol have been proposed as environmental friendly and stable chelating agents for alkaline electroless plating (Norkus E., 2005, Norkus E., 2006). In addition to the complexing agent, biodegradable electrolytes such as methanesulphonic acid are also being explored for use as the bath liquid to enhance conductivity and metal salt solubility and to thus produce uniform coating (Balaramesh P., 2014a, Balaramesh P., 2014b, Balaramesh P., 2014c, Commarieua A., 2002). In this work, we report the properties of an ecofriendly electroless plating process that uses methanesulphonic acid bath liquid, polyhydroxylic complexing agents and glycine as the stabilizer. The surface morphologies of copper deposits produced using such baths are investigated by physical and electrochemical methods.

### MATERIALS AND METHODS

An environmentally friendly bath for electroless deposition of copper was prepared using methanesulphonate, xylitol, para-formaldehyde, potassium hydroxide (to control the pH of the bath), and glycine. Electroless Cu deposition was performed on a Cu sheet (2.0 × 2.0 × 0.1 cm) in a 100 mL beaker. Before deposit, the Cu substrate was rinsed with double distilled water after polishing with fine grid paper. A scoring process was used to clean the precleaned substrates

# International Conference on Science Technology Engineering & Management [ICON-STEM'15]

Journal of Chemical and Pharmaceutical Sciences

ISSN: 0974-2115

using KOH solution. After rinsing with distilled water, surface etching was performed using a solution of  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$  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  $\text{SnCl}_2$  solution ( $\text{SnCl}_2$  mixed with HCl) and activated using HCl solution of  $\text{PdCl}_2$ .

**Calculation for rate and thickness of copper deposits:** The rate of the electroless copper deposit was calculated using the following equation

$$\text{Rate of deposition } (\mu\text{m} / \text{h}) = \text{Thickness} / \text{Deposition time}$$

From the weight of the deposit, total plated area and density of the copper, thickness was calculated as follows.

$$\text{Thickness } (\mu\text{m}) = \frac{W \times 10^4 \times 60}{A \times D}$$

**Table.1. Bath compositions of copper methanesulphonate saccharose and xylitol plain bath with glycine stabilizers (1 ppm)**

Bath contains	Saccharose plain bath	Stabilizers used bath	Xylitol Plain bath	Stabilizers used bath
CuMS (II) ion contacting salt	3 g/L	3 g/L	3 g/L	3 g/L
Saccharose	20 g/L	20 g/L	-	-
Xylitol	-	-	20 g/L	20 g/L
HCHO	10 g/L	10 g/L	10 g/L	10 g/L
KOH (pH)	12.75	12.75	13.25	13.25
Temperature	30 °C	30 °C	30 °C	30 °C
Glycine (stabilizer)	0 ppm	1 ppm	0 ppm	1 ppm

**Characterization of coating surface:** Atomic force microscope (AFM) (NanoSurf Easy Scan2, Switzerland) was used to analyze the surface roughness of the Cu deposits. X-ray diffraction, (X'Pert-Pro, P-analytical) was used to identify the structural properties of the copper deposits. The Debye-Scherrer (1916 &1917) equation for calculating the particle size is given by,

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

Specific surface area of the copper deposits is determined by the formula.

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

**Electrochemical studies:** Cyclic voltammetric curves were obtained using a standard electrochemical analyzer (CHI-600D Austin USA). The copper methanesulphonate solution was deaerated with nitrogen gas. The counter electrode was platinum wire and reference electrode was Ag/AgCl with saturated KCl solution. The voltammograms were recorded at room temperature ( $28 \pm 2$  °C) in 0.1 M  $\text{Na}_2\text{SO}_4$  as supporting electrolyte. Standard glassy carbon electrode was used as working electrode and the voltammograms were recorded in the range of -1.2 to +0.5 V with a scanning rate of 50  $\text{mVs}^{-1}$ . The rate of copper deposits can be determined using deposition current values obtained from the Tafel plots. The copper deposition rate can be calculated using the following ASTM standard equation.

$$\text{deposition rate } (\mu\text{m} / \text{h}) = 3.7328 \times 10^{-4} \left[ \frac{i_{dep}}{\rho} \right] \times Eq. wt$$

## RESULTS AND DISCUSSION

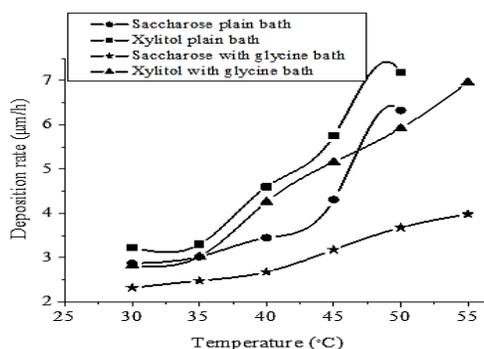
**Effect of temperature on bath condition:** In the plain bath i.e., methanesulphonate bath without addition of stabilizer, deposition rate increased with increase in temperature. However, the bath was stable only up to 40 °C. The bath with stabilizers was stable up to 45 °C. There was a turning point at 45 °C at which the stability of the baths reversed. At elevated temperatures, the whole bath reaction was accelerated to an extent that the deposition reaction was completed within 3-5 hours.

On removing the substrate plate from the bath after the stipulated duration of coating, the excess unused reactants in the bath underwent reduction at a slow phase and copper was found to collect at the bottom of the bath and coat the inner surface of the container. Increasing the concentration of the stabilizer can prolong the stability of the bath.

**Deposition rate and thickness of copper deposits:** Bindra *et.al* 1990 observed that glycine decreases the plating rate and increases ductility and tensile strength for copper deposits in electroless bath. Glycine and formaldehyde form condensation product that reduces the free formaldehyde concentration in the bath, which in turn reduces the plating rate and improves the deposit characteristics. A similar effect was noticed when we used 1 ppm glycine in the methanesulphonate bath. The resulting physical parameter such as deposition rate and thickness of copper deposits also supported this effect.

**Table.2.Effect of temperature on deposition rate and stability of saccharose and xylitol containing methanesulphonate plain bath with glycine stabilizers (1 ppm)**

Temperature (°C)	Saccharose Plain bath	Xylitol plain bath	Bath condition	Saccharose with glycine (1 ppm)	Xylitol with glycine (1 ppm)	Bath condition
	Deposition rate (µm/h)			Deposition rate (µm/h)		
28±2	2.87	3.23	Stable	2.32	2.82	Stable
35	3.02	3.30	Stable	2.48	3.02	Stable
40	3.45	4.60	Stable	2.68	4.26	Stable
45	4.31	5.75	Less stable	3.16	5.18	Stable
50	6.32	7.18	Un stable	3.68	5.92	Less stable
55	-	-	-	3.98	6.96	Un stable



**Figure.1. Effect of temperature on saccharose and xylitol containing methanesulphonate plain bath with glycine stabilizers (1 ppm)**

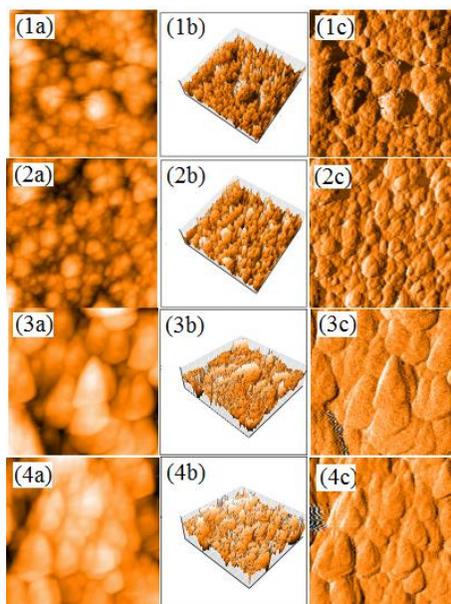
**Surface morphology and structural property:** AFM images of copper deposits on methanesulphonate baths with saccharose and xylitol and with and without glycine as stabilizer were studied. The (a) topography (b) 3-D image and (c) surface area of the deposits were observed. The saccharose plain bath produced maximum roughness of 340 nm. The deposits were dark brown for saccharose baths without stabilizers. However, on addition of 1 ppm of glycine, the deposits became semi bright. Xylitol plain bath produced bright copper deposits with a roughness value of 303 nm.

The structures of copper deposits change with the solution compositions and the plating rate. Junginger *et al.* (1988) suggested that the preferred orientation and structure of the deposits can be explained in terms of the surface free energy of the film and kinetic factors. It was proposed in the case of FCC copper films that the atoms are arranged along the plane with the lowest surface energy, i.e., (111) plane. However, the presence of methanesulphonate resulted in a larger number of copper ions, because of high conductivity and solubility leading to (200) plane. Moreover, increase of the over potential favors the growth of (200) plane which is of relatively lower surface energy than (220) plane and the growth of (111) plane is suppressed by the addition of the methanesulphonate ion. The crystallite size of the copper deposits can be estimated using Debye-Scherrer's equation the specific surface area value is proportional to line width (FWHM) and inversely proportion to the crystallite size. The changes in crystal morphology may be attributed to the presence of hetero compound like nitrogen. Since stabilizers are typically electron donors, and increased chemisorptions of the metal on their surface results in finer deposits and compact structure. Table 3 shows that the results of the crystallite size and specific area were in good agreement with AFM studies.

# International Conference on Science Technology Engineering & Management [ICON-STEM'15]

**Electrochemical studies:** During cyclic voltammetry, the inhibiting effect of stabilizers results in low anodic peak potential value. The low-energy oxidation process is enhanced by the stabilizers. The appearance of a sharp peak indicates that the rate of oxidation is high. High anodic peak current values also indicate that the stabilizer inhibits the deposition of copper. The anodic peak potential values and anodic peak current values describe the quality and quantity of deposits.

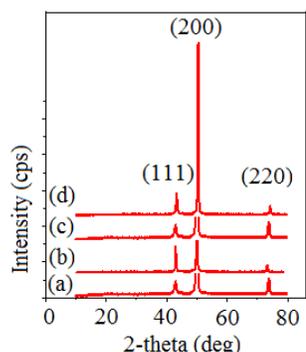
Tafel polarization plot is another way to calculate the deposition rate by using mixed potential theory. Onho *et al.* (1985) determined the mechanism of deposition rate by an electrochemical polarization method that involves obtaining the  $E_{corr}$  and  $I_{corr}$  values from the Tafel plot and applying it to the ASTM standard equation. The  $I_{corr}$  value of glycine was lower than those of saccharose and xylitol plain bath.  $E_{corr}$  values also supported the shift of the potential towards negative values and confirmed the inhibiting property of glycine. These results are in good agreement with weight gain studies.



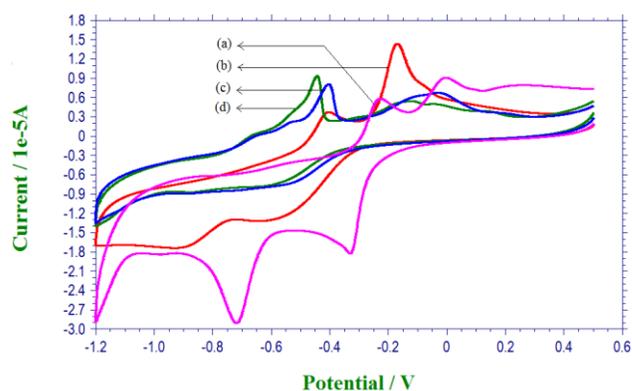
**Figure.2.**AFM images of copper deposits on methanesulphonate baths (a) topography of copper deposits (b) 3-D image and (c) surface area; (1a,1b,1c) - saccharose plain bath, (2a,2b, 2c) - xylitol plain bath, ; (3a,3b,3c) - saccharose plain bath with glycine (1 ppm), (4a,4b, 4c) - xylitol plain bath with glycine (1 ppm)

**Table.3.** Influence of various surface morphologies of saccharose and xylitol plain bath with glycine stabilizers (1 ppm) on electrolysis copper bath.

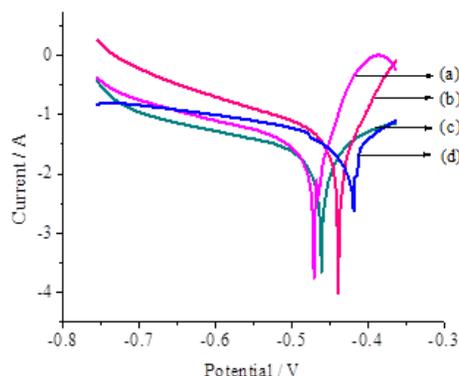
Surface morphologies	Saccharose Plain bath	Xylitol plain bath	Saccharose with glycine (1 ppm)	Xylitol with glycine (1 ppm)
Anodic current value ( $I_{pa-1}$ ) (A)	$1.086 \times 10^{-5}$	$5.924 \times 10^{-6}$	$8.043 \times 10^{-6}$	$3.813 \times 10^{-6}$
Anodic potential value ( $E_{pa-1}$ ) (V)	-0.2354	-0.2275	-0.4044	-0.4040
Crystallite size (nm)	131	126	165	152
Deposition rate ( $\mu\text{m/h}$ )	2.87	3.23	2.32	2.82
Deposition rate ( $\mu\text{m/h}$ ) (Tafel)	0.497	0.543	0.244	0.253
$E_{corr}$ value	-481.28	-441.77	-490.15	-473.50
$I_{corr}$ value	37.55	41.01	18.47	19.09
Roughness value (nm)	340	303	208	142
Specific surface area ( $\text{m}^2/\text{g}$ )	5.112	5.315	4.058	4.406
Thickness ( $\mu\text{m}$ )	172.2	193.8	139.2	169.2



**Figure.3. XRD pattern of copper deposits on methanesulphonate bath (a) saccharose plain bath. (b) saccharose plain bath with glycine (1 ppm) (c) xylitol plain bath (d) xylitol plain bath with glycine (1 ppm)**



**Figure.4. Cyclic voltammogram for electroless copper methanesulphonate bath (a) saccharose plain bath with glycine (1 ppm), (b) xylitol plain bath with glycine (1 ppm), (c)- xylitol plain bath, (d) saccharose plain bath**



**Figure.5. Tafel polarization curve for electroless copper methanesulphonate (a) xylitol plain bath with glycine (1 ppm), (b) xylitol plain bath, (c) saccharose plain bath with glycine (1 ppm) (d) saccharose plain bath**

## CONCLUSION

Biodegradable glycine has been found to act as stabilizers on polyols containing electroless copper bath. 1 ppm addition of glycine was used in a saccharose bath optimized at pH of 12.75 and in a xylitol bath at pH 13.25. Glycine has been found to increase the crystallite size of the copper deposits, greatly inhibit the bath and extend its life. The use of KOH increases the solubility of  $\text{Cu}(\text{OH})_2$  and no precipitates were observed during plating. Glycine reduces the roughness of the coated copper surface. Addition of small volume of MSA as bath liquid increases the number of copper ions in solution, because of high conductivity and solubility leading to formation of the (200) plane. Deposition rate, quality and quantity of the ecofriendly bath and coated copper deposits were determined by electrochemical CV and Tafel polarization studies.

## REFERENCES

- Balaramesh P, Venkatesh P and Rekha S, The effect of stabilizers on electroless copper plating from saccharose containing methanesulphonate baths, *Asian journal of science and technology*, 5, 2014, 276-280.
- Balaramesh P, Venkatesh P and Rekha S, Influence of imidazole and benzotriazole on electroless copper plating, *Surface engineering*, 30, 2014, 552-556.
- Balaramesh P, Venkatesh P, Rekha S, and Hemamalini M, Bath parameters affecting electroless copper deposition-A review, *International journal of innovative research and studies*, 3, 2014, 167-181.
- Bindra P, and White J, Fundamental aspects of electroless copper plating, In *electroless plating: Fundamentals and applications*, G. O. Mallory and J. B.Hajdu, Eds, American electroplaters and surface finishers society, 327, 1990.
- Commarieua A., Hoelderich W., Laffitte J.A., and Dupont. M.P, Fries rearrangement in methane sulphonic acid, an environmental friendly acid, *J. Mol. Catalysis A: Chemical*, 182, 2002, 137-141.