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RESEARCH ARTICLE

THE EFFECT OF STABILIZERS ON ELECTROLESS COPPER PLATING FROM SACCHAROSE-CONTAINING METHANE SULPHONATE BATHS

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ABSTRACT

The effect of addition of 2-Mercaptobenzothiazole (2-MBT), Thiourea, N-Methyl thiourea and 2,2'-dipyridyl on electroless copper deposition from a methane sulphonate bath are studied. Saccharose and Para formaldehyde are used as the complexing and reducing agents respectively. All the stabilizers are found to improve the bath stability and produce the quality deposits. Of the four stabilizers studied, 2,2'-dipyridyl produces brightest copper deposits with more compact and finer sized crystals than other stabilizers. The crystal structure and surface morphology are observed and supported by SEM, AFM and XRD studies.

INTRODUCTION

Electroless deposition is considered to be more attractive than electroplating. It has very high selectivity, uses a very thin seed layer, has excellent step coverage, good trench filling capacity and does not need electrical contacting of wafers during deposition. Electroless plating of copper metal possesses advantages such as excellent solderability, possibility of plating even at room temperature and high conductivity than other metals. Thus it has been successfully employed in electronics fabrication. The theoretical basis of electroless copper deposition process has been studied by Pearlstein in Lowenheim's book (Lowenheim, 1974), and reviewed and developed further by Goldie (1968) and Saubestre (1962). Various common complexing agent including EDTA, Triethanolamine, Ethylenediamine, Tartrate, Quadral and Trisodium salts have been used in the electroless plating bath. Among these, EDTA has been found to be having excellent chelant property over a wide pH range (Paunivic, 1968; Lee, 1987; Lukes, 1964; Dumesic, 1974; Pearlstein and Weigtman, 1973; Schoenberg, 1972; Balakrishma and Mahapatra, 1973). The EDTA bath shows dual chelating property (i.e.) it avoids cupric hydroxide precipitation and maintains the stability of electroless plating. However EDTA is not very bio-degradable, forms complexes with heavy metals increases the total nitrogen content of waste water and produces serious pollution problems in waste water (Narcus Chimija, 2006; Narcus and Prusinskas, 2007). Polyhydroxylic compounds, such as Xylitol, D-mannitol, D-sorbitol, Alditol, and Saccharose have been proposed as environmentally friendly alternate copper (II) ligands for electroless copper plating solutions (Norkus and Vaskelis, 2005).

Formaldehyde has been the most commonly used reducing agent in electroless copper solution for deposition of high purity copper in through hole plating (THP) of printed circuit boards (PCBs). These reducing agents have been found to play a vital role in kinetics of the overall reaction (Molenaar *et al*., 1974; Lax and Maugham, 1979; Van Den Meerakar, 1981; Bindra and Roldan, 1985; Tam, 1985; Paunovic, 1951; Shumacher *et al*., 1951; Gottesfeld *et al*., 1986). More recently, methane sulphonic acid (MSA) has gained popularity in electroless plating in the electronics industries. Addition of small volume of methane sulphonic acid has been reported to produces uniform and high quality deposits (Rekha *et al*., 2010). The kinetics associated with the use of stabilizing additives has been discussed by Bielinski and Kaminski (1987). 2,2'-dipyridyl has been reported to reduce the rate of the copper deposition in formaldehyde-based electroless copper plating (Andricacos *et al*., 2002) but, the deposit produced using this additive has been found to be glossy with

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good tensile strength and ductility (Kondo *et al*., 1999). In this work, a new bath based is studied wherein ecofriendly copper methane sulphonate is used instead of copper sulphate as the plating solution. Advantage of using methane sulphonate bath includes better metal solubility, higher conductivity and easier effluent treatment. Saccharose and paraformaldehyde are used as the complexing and reducing agents respectively and 2-MBT, Thiourea, N-Methyl thiourea and 2,2-dipyridyl as stabilizers. The characteristics of the copper deposits formed using the above bath is established.

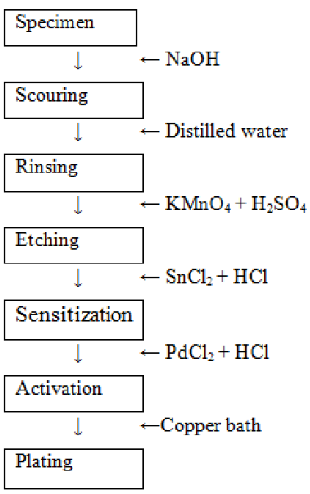
Experimental

Chemicals and solutions

1. Copper as methane sulphonate-3g/lit: synthesized in-house from copper carbonate
2. Saccharose-20g/lit
3. paraformaldehyde-10g/lit
4. KOH-up to pH needed
5. Temperature-28±2˚C
6. Stabilizers-Required quantity

Copper surface formation

The plating experiments were performed on a pure copper sheet (2.0 X 2.0 X 0.1 cm). The copper plate was polished by fine grit paper, rinsed with double distilled water and subjected to the following procedure. The Multisteps - Process was carried out for electroless copper plating



The electroless copper plating experiment was performed for 60 minutes at 30˚C in a 100 ml glass beaker. The amount of copper deposited was determined by mass difference. All measurements were repeated at least three times and amount of copper deposited was calculated by the weight gain method.

The rate of deposition (μm/h) = (W X $10^{4)}$ / D A T
W-Weight of deposit (g)
D-Density of the deposit (g/cm^3)
A-Surface area of the plates (cm^2)
T-Plating duration (hr)

Preparation of stock solution

About 50g of copper carbonate was weighed and transferred into a 500 ml clean beaker and treated with approximately 60 ml of methane sulphonic acid until evaluation of carbon-di-oxide gas. Minimum quantity of double distilled water was added and the solution was made up to 250 ml in a standard measuring flask. The oil and suspended impurities present in the solution were removed by filtration and the solution was stored in a clean container. One ml of stock solution was analyzed using N/10 of standard sodium thio sulphate and the amount of copper was calculated.

Characterization of surface

The surface morphology of electroless copper deposited plates was examined by SEM analysis. The crystal structure of the copper deposits was investigated from XRD studies and the roughness of the deposits was characterized by AFM studies.

RESULTS AND DISCUSSION

Saccharose containing methane sulphonate bath produced stable complexes with copper (II) ion in alkaline solutions. The plating process started at pH above 12 and optimum deposition rate was observed at pH 12.75, beyond which the deposition slowed down. In the absence of stabilizers, the rate of plating was poor. The effect of addition of small amount of stabilizers like 2-MBT, Thiourea, N-Methyl thiourea, and 2,2'-dipyridyl on the rate of deposition and bath stability were studied as follows.

Table 1. Effect of concentration of stabilizer and copper deposits on saccharose-containing methane sulphonate bath MSCu (II)-3g/lit, Sa-20g/lit, HCHO-10g/lit, pH-12.75, stabilizers-2-MBT bath, Thiourea bath, N-Methyl thiourea bath and, 2,2'dipyridyl bath

Concentration (ppm)	Deposition rate(μm/h)			
	2-MBT	Thiourea	N-Methyl thiourea	2,2'-dipyridyl
10	1.43	1.14	1.58	1.72
5	2.01	1.72	2.16	2.30
1	2.44	2.58	2.64	2.73
0.5	2.53	2.62	2.73	2.76
0.1	2.58	2.72	2.79	2.81

The stabilizers were more stable and optimized at 1 ppm concentration. 2-MBT and Thiourea were found to reduce the rate of copper deposition. At low concentration of stabilizers, copper deposition increased, but at very low concentration there were no significant changes in copper deposition.

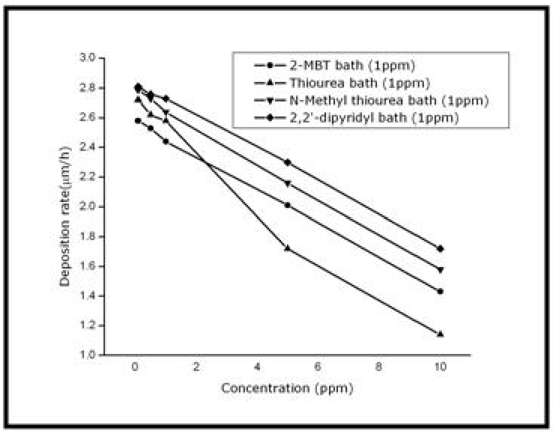


Figure 1. Effect of concentration of stabilizer and copper deposits on saccharose-containing methane sulphonate bath MSCu (II)-3g/lit, Sa-20g/lit, HCHO-10g/lit, pH-12.75, stabilizers-2-MBT bath, Thiourea bath, N-Methyl thiourea bath and, 2,2'dipyridyl bath

The inhibiting effect of stabilizers followed the following pattern.

2-MBT & Thiourea > N-methyl thiourea > 2,2'-dipyridyl

The stabilizers 2-MBT and Thiourea produced deposits with similar characteristics such as color, stability and crystal structure. N-Methyl thiourea and 2,2'-dipyridyl produced deposits with similar color, stability and crystal structure.

The surface morphology was studied by SEM analysis. The inhibiting effect of plating rate may be due to the presence of hetero atoms nitrogen and sulphur in 2-MBT and Thiourea respectively (Hung, 1985). The stabilizer N-Methyl thiourea produces smooth deposits that are brighter than deposits found using 2-MBT and 2,2'- dipyridyl stabilizers due to methyl substituent.

Table 2. Effect of Temperature copper deposits on saccharose-containing methane sulphonate bath MSCu (II)-3g/lit Sa-20 g/lit HCHO-10 g/lit, pH-12.75, Stabilizers- 2-MBT- (1ppm), Thiourea (1ppm), N-Methyl thiourea (1ppm) and 2,2'dipyridyl (1ppm)

Temperature (˚C)	Plain bath		Stabilizers (1ppm) concentration				
			2-MBT bath	Thiourea bath	N-Methyl thiourea bath	2,2'-dipyridyl bath	Stability
	Deposition rate (µm/h)	Stability	Deposition rate (µm/h)	Deposition rate (µm/h)	Deposition rate (µm/h)	Deposition rate (µm/h)	
28±2	2.85	Stable	2.44	2.58	2.64	2.73	Stable
35	2.57	Stable	2.58	2.61	2.70	2.76	Stable
40	3.45	Stable	2.70	2.73	2.87	3.16	Stable
45	4.31	Less stable	3.21	3.30	3.45	4.02	Stable
50	6.32	Un Stable	3.74	4.02	4.74	5.17	Less stable
55	-	-	4.02	4.31	5.46	5.75	Un Stable

The effect of temperature on saccharose containing methane sulphonate bath with stabilizers was examined. Table (2) illustrates that the bath was stable upto 45˚C, less stable at 50˚C and unstable at higher temperature. At 45˚C the deposition rate, stability and crystal structure were found to be variable.

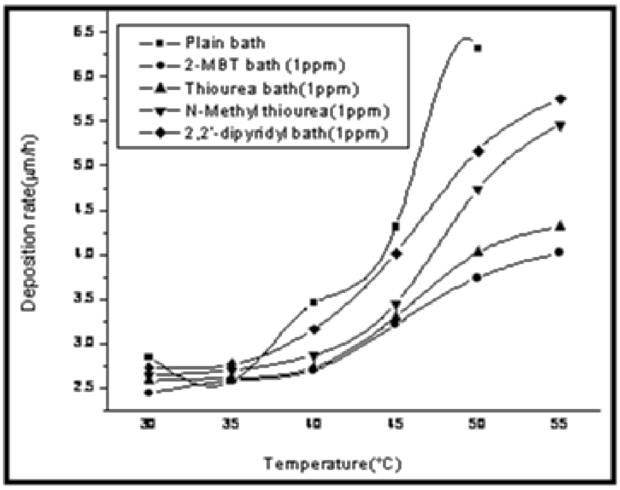
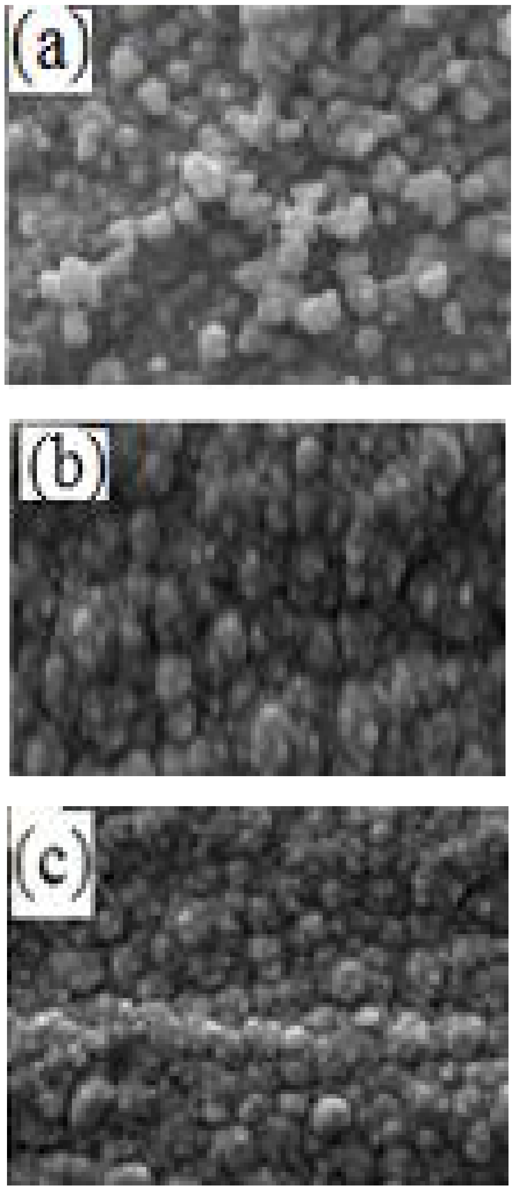
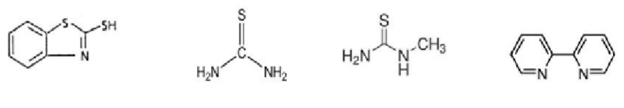


Figure 2. Effect of Temperature on copper deposits in saccharose-containing methane sulphonate bath MSCu (II)-3g/lit Sa-20 g/lit HCHO-10 g/lit, pH-12.75, using Stabilizers 2-MBT- (1ppm), Thiourea (1ppm), N-Methyl thiourea (1ppm) and 2,2'dipyridyl (1ppm)



The copper deposits were seen to have a fine grained structure at room temperature and coarser grain structure was observed at high temperature. The chemical structures of stabilizers used in this work are given below for better understanding of the properties.



2-Mercaptobenzothiazole thiourea N-Methyl thiourea 2,2'-dipyridyl

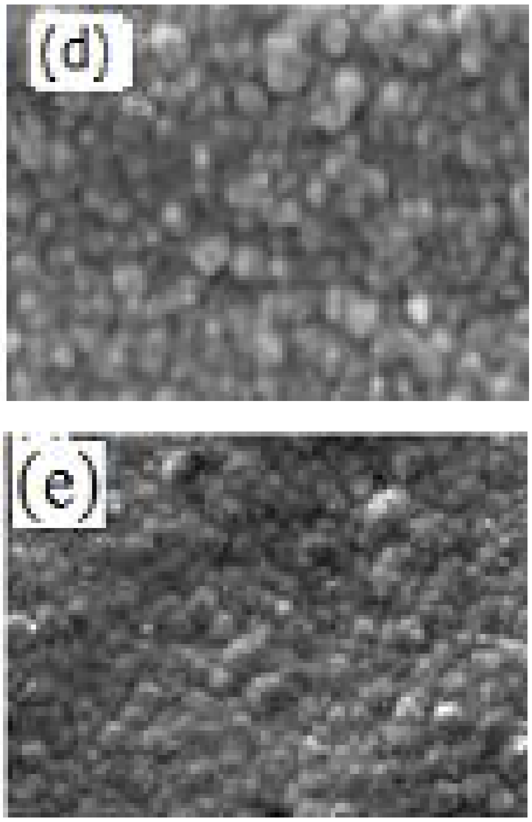


Figure 3. SEM images of copper deposits saccharose-containing methane sulphonate bath MSCu (II)-3g/lit, Sa-20 g/lit, HCHO-10g/lit, pH-12.75, a) Plain bath (i.e) stabilizer-(0- ppm) b) 2-MBT (1-ppm), c) Thiourea (1ppm), d)N-Methyl thiourea (1ppm) and e) 2,2'dipyridyl (1- ppm)

The stabilizer 2,2'-dipyridyl was found to have favorable effect on electroless deposition of copper from methane sulphonate bath. 2,2'-dipyridyl inhibit the catalytic oxidation reaction and presence of delocalized π-electron in its structure produces bright deposits with uniform, compact and fine structure. Atomic force microscopy (AFM) studies shows explain that the color of copper deposits is dark brown when deposited from the plain bath, and baths containing 2-MBT bath and thiourea. But N-Methyl thiourea and 2,2dipyridyl bath produced semi-bright copper deposits. The following AFM images, (a) the topography of copper deposits, (b) 3-D images and (c) surface area show the roughness of the deposits. The crystal orientations and lattice parameters for the deposits were studied by XRD. Lee *et al* (1996) had earlier concluded that copper methane sulphonate bath furnished more number of copper ions, because of high conductivity and solubility leading to (200) plane. The copper deposits on saccharose-containing methane sulphonate plain bath, and all stabilizers show the preferred orientation of (200) plane. The crystallite size of the copper deposits can be estimated using the Debye-Scherer's equation (Mastsuoka *et al*., 1992; Cullity, 1978).

$$D = K\lambda/\beta\cos\theta \qquad (1)$$

Where,
λ –wavelength of Cu Kα
β –Breadth of diffracted line (i.e) FWHM (rad)
θ –Bragg angle of diffracted rays
K – Constant (0.89)

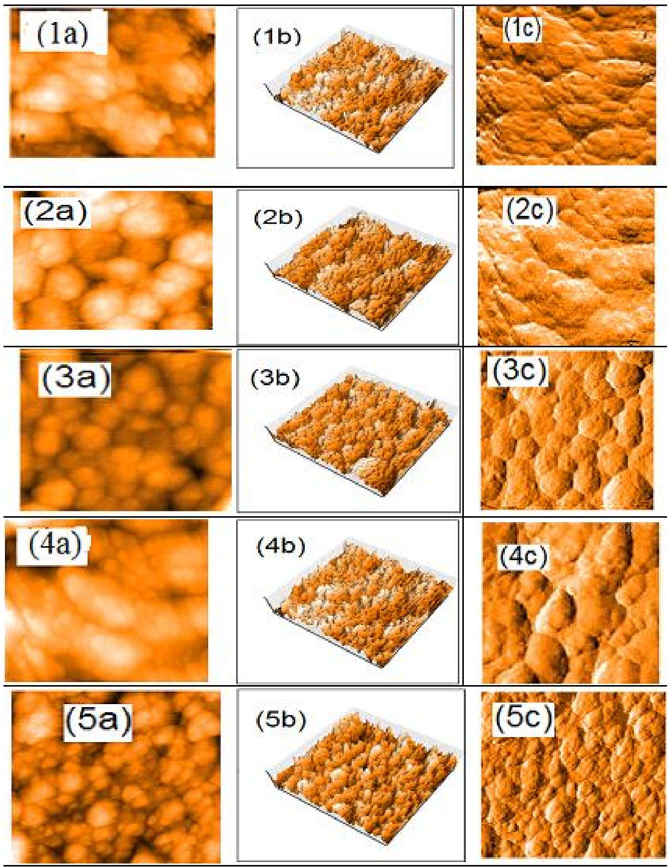


Figure 4. AFM images of copper deposits saccharose-containing methane sulphonate bath MSCu (II)-3g/lit, Sa-20 g/lit, HCHO-10 g/lit, pH-12.75, a) Topography of the copper deposits b) 3-D image c) surface area roughness. (1a,1b,1c)- Plain bath, (2a,2b,2c)- 2-MBT, (3a,3b,3c)- Thiourea, (4a,4b,4c)- N-Methyl thiourea, (5a,5b,5c)- 2,2dipyridyl

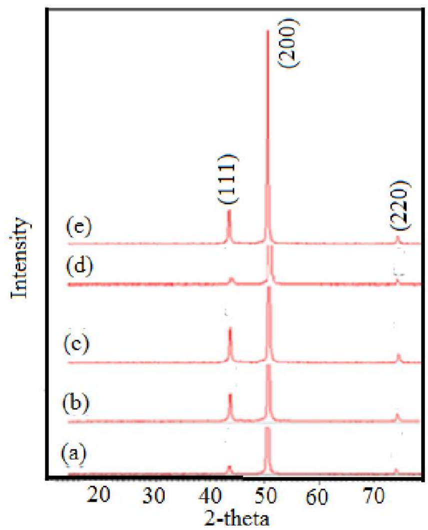


Figure 5. XRD images of copper deposits saccharose-containing methane sulphonate bath MSCu (II)-3g/lit Sa-20 g/lit HCHO-10 g/lit, pH-12.75, (a) Plain bath (b) 2-MBT (c) Thiourea (d) N-Methyl thiourea (e) 2,2dipyridyl

Table 3 shows the crystallite size of copper deposits on saccharose-containing methane sulphonate plain bath, 131.31 nm for plain bath, 133.48 nm for 2-MBT bath, 133.40 nm for Thiourea bath, 130.62 nm for N-Methyl thiourea bath and 128.58 nm for 2,2'dipyridyl bath. The crystallite size was larger in bath containing 2-MBT and thiourea than the those from the plain bath, but smaller when N-Methyl thiourea and 2,2'dipyridyl were used as additive.

Table 3. Characteristic peak relative intensities and crystallite size of the copper deposits. (1) Plain bath (2) 2-MBT bath (3) Thiourea bath (4) N-Methyl thiourea bath (5) 2,2dipyridyl bath

S.no	Name of the bath	Crystallite size	Intensity (111) plane	Intensity (200) plane	Intensity (220) plane
1	Plain bath	131.31	2.40	100	2.39
2	2-MBT bath (1-ppm)	133.48	12.12	100	3.67
3	Thiourea bath (1ppm)	133.40	9.52	100	4.11
4	N-Methyl thiourea bath (1ppm)	130.62	12.15	100	4.22
5	2,2'Dipyridyl (1-ppm)	128.58	13.72	100	4.27

Conclusion

The autocatalytic reduction of Cu (II) by formaldehyde from a solution of saccharose –containing copper methane suphonate ligand starts at pH above 12, reaches maximum at pH 12.75, then slows down again at higher pH. Addition of 2-Mercaptobenzothiazole (2-MBT), Thiourea, N-Methyl thiourea and 2,2'-dipyridyl to the bath decreases the plating rate and extends the bath life time. AFM and SEM studies of the deposits formed in 2-MBT and Thiourea containing bath show the deposits to be dark brown in color, with larger grain sizes than deposits from the plain bath. The copper deposits from baths containing N-Methyl thiourea and 2,2' dipyridyl bath are brightner and of smaller grain sizes. XRD studies validate crystallite size of the copper deposits in all cases. The deposits are found to have higher (200) plane orientation. 2,2' dipyridyl containing bath produces bright deposits with, uniform, compact and fine structure.

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