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Effect of Thio Derivatives on Electroless Copper Methanesulphonate Bath

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Abstract: Environmental concerns have led to interest in developing cyanide and EDTA-free methanesulphonate baths for electroless deposition of copper. Polyhydroxylic complexing agents such as xylitol can be used instead of EDTA in such baths and para formaldehyde as the reducing agent. In this work, we study the effects of stabilizers such as thiourea, *N*-methylthiourea, phenylthiourea and diphenylthiourea in such baths. The electroless deposition was carried out at the optimum *p*H of 13.25. Shape and roughness values of copper films produced were analyzed by SEM and AFM analyses. The nano crystallite size and specific surface area were characterized by XRD observation. The electrochemical characteristics were studied by cyclic voltammetry to understand the role of the stabilizers in electroless deposition. Corrosion kinetics parameters were analyzed by Tafel and impedance studies. Methanesulphonate baths that contain N-methylthiourea as stabilizer were found to perform best in terms of the quality and quantity of deposits produced.

Key words: copper sulphate, reducing agent, stabilizer, thin film, thiourea.

Introduction

Electroless plating of copper is considered to be better than electroplating because of advantages of improved solution stability, uniform plating thickness, excellent step coverage, good filling capacity and absence of need for electrical contacting of wafers during deposition. There have been significant advancements in this technology in the past decade and it is now being used widely in applications such as fabrication of decorative articles,¹ semiconductors, integrated circuits and through hole plating in printed circuit boards.²⁻⁵ Emerging applications of this technique lie in areas of electromagnetic interference shielding materials,⁶ ceramic or polymeric nanoparticles, energy conversion, aerospace, biomedical and automotive industries⁷

Conventional electroless copper plating uses baths of copper sulphate with additives such as EDTA and cyanide that pose problems of toxicity and non-biodegradability. In 1950, Procell⁸ recognized the use of the Bronsted acids, alkylsulphonic acids for electroplating applications instead of copper sulfate/cyanide baths. Alkylsulphonic acids with one and five carbon atoms in the alkyl group form water soluble salts of various metals and can potentially be used in electroless plating. This system however gained commercial acceptability only during the early 1980's and methanesulphonic acid (MSA) became a potential electrolyte for use in various metals coating applications.⁹⁻¹¹

MSA's superiority over other bath liquids arises from its excellent metal salt solubility, stability, biodegradability, excellent conductivity, and ease of disposal. Another attractive feature of MSA baths is that, the bath can be operated at room temperature.¹² Addition of small amounts of MSA has been reported to produce uniform and high quality coatings. However, literature survey shows that, not much work has been carried out to understand and optimize bath conditions. Conventionally, ethylenediaminetetraacetic acid (EDTA) has been used as the complexing agent in electroless copper baths, but its environmental pollution issues necessitate development of better and safer complexing agents.¹³⁻¹⁸ Polyhydroxy compounds (polyols), which were reported in the late 20^{th} century to form chelates with Cu(II) ions in alkaline medium are potential replacements to EDTA. They are well suited for copper electroless plating because they form stable complexes with copper (II) ions in alkaline solutions. This minimizes the amount of free Cu(II) in the solution, and thus prevents the precipitation of Cu(OH)₂ and improves quality of copper plating.

Polyhydroxylic compounds are not only biodegradable, but also completely non-toxic in that many of them are found in the human metabolic cycle and are safely used in a large number of applications as seen in Figure 1.



Figure 1. Flow chart for xylitol and its applications

Thus, natural polyols such as xylitol could be eco friendly alternatives to EDTA currently used as complexing agents in electroless copper baths. ^{19,20} In this work, we have studied the electroless plating characteristics of xylitol containing methane sulphonate baths at the optimum deposition pH of 13.25 and the effects of various stabilizers on the bath performance. The effect of stabilizers such as thiourea, *N*-methylthiourea and diphenylthiourea have been carefully examined studied and correlated.

Experimental

The following chemicals were used for the study:

Chemicals and solutions

(i) Copper as methane sulphonate -3 g/L: synthesized in-house from copper carbonate
(ii) Xylitol-20 g/L
(iii) Para formaldehyde-10 g/L
(iv) KOH-upto pH 13.25
(v) Temperature-28 ± 2 °C
(vi) Stabilizers-1 ppm

An environmentally friendly bath for electroless deposition of copper was prepared using methanesulphonate, xylitol, para–formaldehyde, and potassium hydroxide (to vary the *p*H of the bath), with added stabilizers (thiourea, *N*-methylthiourea, phenylthiourea and diphenylthiourea). The electroless Cu deposition was performed on a Cu sheet $(2.0 \times 2.0 \times 0.1 \text{ cm})$ 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 using KOH solution. After rinsing with distilled water, surface etching process was performed 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 a HCl solution of PdCl₂.

Calculation for rate and thickness of copper deposits

Rate of the electroless copper deposit was calculated using the following equation

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

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

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

where,

 $W = (w_1-w_2) =$ Weight of deposit in gram $w_1 =$ Weight after plating $w_2 =$ Weight after stripping A = Total plated area of the substrate (cm²) D = Density of the copper (g/cc)

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^{24,25} for calculating the particle size is given by

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

where, K is the Scherrer constant, λ is the wavelength of light used for the diffraction, β is the 'Full Width Half Maximum' of the sharp peaks and θ is the angle measured. 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 formula

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

where ρ is the crystallite size (nm) and d is the theoretical density of copper (8.96 g/cm3).

Electrochemical studies

Cyclic voltammetric curves were obtained using 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 ± 2 °C in 0.1 M Na₂SO₄ as supporting electrolyte. Standard 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 0.1 M Na₂SO₄ supporting electrolyte solution was kept at *p*H 13.25 using a KOH solution for xylitol bath. The anodic peak potential value and anodic peak current values describe the quality and quantity of deposits.

Tafel plots give a direct measure of the corrosion current, which can be related to corrosion rate. This technique is faster and more accurate than weight loss measurements. Polarization data with the Tafel constant are used to find the corrosion rates. Electrochemical impedance spectroscopy (EIS) is a traditional method, central to electrochemical science and electrochemistry and studies interfacial charge transfer between a solid conductor (the working electrode, WE) and an electrolyte. This was performed by applying a voltage between the WE and CE, ad using a reference electrode (RE), it was possible to identify the voltage drop at the interface between the WE and the electrolyte. There are around 140 electrical equivalent circuits available in electrochemical impedance spectroscopy. The following electrical equivalent circuit was found to match the system.





where,

 $C_1 \& C_2$ - Double layer capacitances $R_1 \& R_2$ - Charge transfer resistances

To make an EIS measurement, a small amplitude signal, usually voltage between 5 and 50 mV was applied to a specimen over a range of frequencies from 10 mHz to 10 KHz. The EIS instrument recorded the real (resistance) and imaginary (capacitance) components of the impedance response of the system. Depending upon the shape of the EIS spectrum, a circuit description code and initial circuit parameters were used to find the charge transfer resistance and double layer capacitance value.

Results and discussions

Deposition rate and thickness of copper deposits

In general, the complexation of stabilizer with copper ions may cause greater inhibiting effects. Thus, as seen in table 1, thiourea resulted in lower deposition rates than the plain bath. The remaining three stabilizers increased deposition rates over the plain bath and were accelerators in the xylitol bath. N-methylthiourea showed least acceleration and the deposition value was only very slightly more than the xylitol plain bath. The deposition rates were determined using physical weight gain method and electrochemical Tafel polarization technique.

Table 1. Deposition rate and thickness of copper deposits on optimized methanesulphonate xylitol plain bath with stabilizers

S.No.	Xylitol plain bath with stabilizers	Deposition rate	Thickness	
	(1 ppm)	(µm/h)	(µm)	
1	Plain bath	3.23	193.8	
2	Thiourea	3.02	181.2	
3	N-methylthiourea	3.51	210.6	
4	Phenylthiourea	3.88	232.8	
5	Diphenylthiourea	4.02	241.2	

The thickness of deposition increased on increasing plating time duration on electroless copper plating. This was determined by using simple gravimetric formula. The thickness value gradually increased from thiourea to diphenylthiourea. On comparing with plain bath, thickness of deposits on using thiourea produced lower value and *N*-methylthiourea to diphenylthiourea gave higher values. These thickness results are in good agreement with deposition rate, and confirmed the inhibiting and acceleration properties of stabilizers.

Quality and quantity -Cyclic voltammetry (CV)

Quality and quantity of the copper deposits were analyzed by cyclic voltammetry studies. Nature of the bath, presence of stabilizer, appearance of peak, anodic peak potential value and anodic peak current values were analyzed. Table 2 shows that thiourea strongly inhibited the oxidation process and produced lower anodic peak potential value than xylitol plain bath and the other stabilizers used in this bath. Charge density, steric and inductive effects were found to alter the potential values. Presence of phenyl group enhanced the plating reaction.

 Table 2. Anodic peak potential and anodic peak current values from cyclic voltammogram for electroless copper methanesulphonate xylitol plain bath with stabilizers

S.No.	Xylitol plain bath with stabilizers	E _{pa-1} values	I _{pa-1} values
	(1 ppm)	(V)	(A)
1	Plain bath	-0.2275	5.924 x10-6
2	Thiourea	-0.2777	8.508 x10-6

3	N-methylthiourea	-0.1999	1.046 x10-5
4	Phenylthiourea	-0.0353	1.246 x10-5
5	Diphenylthiourea	-0.0262	1.205 x10-5



Figure 3. Cyclic voltammogram for electroless copper methanesulphonate xylitol bath at *p*H 13.25; (a) N-methylthiourea bath, (b) thiourea bath, (c) xylitol plain bath, (d) phenylthiourea bath. (e) diphenylthiourea bath.

Nanostructure - Atomic force microscope (AFM)

Surface roughness, shapes, material homogeneity and inner metallic distribution of the copper deposits on xylitol containing methanesulphonate bath were determined by AFM studies. Table 3 shows that, maximum roughness 303 nm was observed for xylitol plain bath and gradually decreased up to *N*-methylthiourea and then increased to diphenylthiourea. This is due to positive inductive effect by methyl group and steric factor. *N*methylthiourea produces brighter deposits than the other stabilizers with very low roughness value, good uniformity, and a compact honey comb structure.



Figure 4. AFM images of copper deposits on methanesulphonate xylitol plain bath (a) topography of copper deposits (b) 3-D image and (c) surface area; (1a,1b,1c) -xylitol plain bath, (2a,2b, 2c)-thiourea bath, (3a,3b,3c)-N-methylthiourea bath, (4a,4b,4c)- phenylthiourea bath, (5a,5b,5c)-diphenylthiourea bath

S.No.	Xylitol plain bath with stabilizers (1 ppm)	Roughness value (nm)	Shape or stucture
1	Plain bath	303	Rocks
2	Thiourea	108	Small grains
3	N-methylthiourea	72	Honey comb
4	Phenylthiourea	114	Small grains
5	Diphenylthiourea	122	Coarse rains

Table 3. Comparison of roughness values of copper deposits on xylitol methanesulphonate plain bath and baths with stabilizers from AFM studies.

DC electrochemical monitoring technique - Tafel polarization (TP)

Corrosion kinetics parameters such as E_{corr} and I_{corr} value were determined by the Tafel polarization technique. Deposition rates were determined using these above Tafel parameters values.²¹ Table 4 that shows the inhibiting and accelerating effect of stabilizers confirmed the results observed using xylitol plain bath. Both physical and electrochemical results of the deposition rate showed similar effects. Thus, there is good agreement in the behavior of stabilizers in xylitol bath.

Table 4. Tafel polarization values of corrosion current, corrosion potential and deposition rate for electroless copper methanesulphonate xylitol plain bath with and without stabilizers

S.No.	Xylitol plain bath	β _a	βc	Ecorr	Icorr	Deposition
	with stabilizer (1 ppm)	V/decade	V/decade			rate (µm/h)
1	Plain bath	51.30	247.7	-441.77	41.01	0.543
2	Thiourea	93.91	554.5	-489.66	27.75	0.367
3	N-methylthiourea	94.67	326.2	-498.68	52.66	0.697
4	Phenylthiourea	156.2	118.3	-528.86	106.7	1.403
5	Diphenylthiourea	184.6	142.7	-542.12	141.9	1.879



Figure 5. Tafel polarization curve for electroless copper methanesulphonate xylitol bath in *p*H 13.25; (a) thiourea bath (b) xylitol plain bath, (c) *N*-methylthiourea (d) phenylthiourea bath and (e) diphenylthiourea bath

AC electrochemical monitoring technique - Electrochemical impedance spectroscopy (EIS)

Interfacial charge transfer between the solid conductor and the electrolyte was investigated using electrochemical impedance spectroscopy.²² The values of charge transfer resistance and double layer capacitance were obtained for xylitol containing electroless copper methanesulphonate bath.

Table 5 indicates the value of C_{dl} is 0.1421×10^{-3} and R_t is 30.23 of xylitol plain bath. The corrosion inhibition efficiency was due to the presence of hetero atom, electron density at donor sites and availability of functional group.

 Table 5. Electrochemical impedance value of charge transfer resistance and double layer capacitance for electroless copper methanesulphonate xylitol plain bath with and without stabilizers

S.No.	Xylitol plain bath with stabilizers (1 ppm)	Double layer Capacitance (C _{dl})		Charge transfer Resistance (R _t)	
		$C_1 \ge 10^{-6}$	$C_2 \ge 10^{-3}$	R ₁	\mathbf{R}_2
1	Plain bath	3.474	0.1421	256	30.23
2	Thiourea	1.125	0.1086	534	52.39
3	N-methylthiourea	2.108	0.0827	292	28.57
4	Phenylthiourea	2.018	0.0855	323	14.05
5	Diphenylthiourea	4.665	0.1888	159	12.76



Figure 6. Nyquist diagram of electroless copper methanesulphonate xylitol bath in pH 13.25

Phase composition - X-ray diffraction (XRD)

Crystallite size is inversely proportional to the specific surface area. Table 6 indicates that the thiourea increases size and decreases the specific surface area of the copper deposits on substrate.²³ This is due to strong complexation with copper ions resulting in greater inhibiting effect. Presence of functional group, molecular area, and molecular weight also played a role. Aromaticity and the effect of delocalized π electron in the phenyl ring may influence the size.

Table 6. Crystallite size and specific surface area of copper deposits for electroless copper methanesulphonate xylitol plain bath with stabilizers.

S.No	Xylitol plain bath with	Crystallite size	Specific surface area
	Stabilizers (1 ppm)	(nm)	(m^2/g)
1	Plain bath	126	5.315
2	Thiourea	134	4.997
3	N-methylthiourea	126	5.315
4	Phenylthiourea	106	6.317
5	Diphenylthiourea	101	6.630



Figure 7. XRD pattern of copper deposits on methanesulphonate xylitol plain bath with thio derivatives stabilizers (1 ppm); (a) thiourea bath (b) xylitol plain bath, (c) *N*-methylthiourea, (d) phenylthiourea bath and (e) diphenylthiourea bath

Conclusion

The effect of stabilizers on electroless copper deposition in xylitol containing methanesulphonate bath with formaldehyde was studied. This bath was optimized at pH 13.25 using KOH adjuster. The effects of 1 ppm concentration of four stabilizers viz., thiourea, *N*-methylthiourea, phenylthiourea and diphenylthiourea were studied and various deposition conditions were discussed. 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 baths.

The size, charged ion characteristics, complexation of stabilizers, and effect of delocalized π electron present in heteroatoms, such as sulphur and nitrogen significantly changed the deposition rate and thickness of copper deposits. The complexation and steric factors of stabilizers may have altered the roughness value. Presence of functional groups in the stabilizer and electron density at donor sites affected the charge transfer resistance and double layer capacitance. Aromaticity and the effect of delocalized π electron in the phenyl ring may have influenced the crystallite size in XRD pattern. Electroless methanesulphonate baths with N-methylthiourea produced brightest copper deposits with better physical and electrochemical properties.

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