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ENHANCEMENT OF DEPOSITION RATE BY ACCELERATORS EMPLOYING D-MANNITOL AS COMPLEXING AGENT

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ABSTRACT. Copper possesses better conductivity which makes it an ideal plating choice for the electronics and semiconductor industries. Copper electroless plating can be carried easily on non-conductors like plastics, ceramics, fabrics, glasses etc. One of the limitations of electroless plating is its very low plating rate, which is further reduced by the addition of stabilizers which is quite essential for the plating process. A stabilizer improves stability of bath and deposit qualities, but slows down the plating rate. The current study focuses on the enhancement of plating rate by the addition of accelerators in eco-friendly copper methane sulphonate bath. It is observed that accelerators like guanidine hydrochloride and 2,6-diaminopyridine improves the rate of deposition with good deposit quality. It was studied with weight gain method and analyzed with tafel polarization studies. The surface of the deposit was analyzed with X-ray diffraction (XRD) and scanning electrode microscope (SEM).

KEY WORDS: Copper, Methane sulphonic acid, Accelerators, Guanidine hydrochloride, 2,6-Diaminopyridine

INTRODUCTION

Electroless plating finds application in the field of printed circuit boards, integrated circuits and also in electromagnetic shielding as it can be carried out at room temperature. Electroless plating is a chemical deposition carried out by reducing agent onto the active surface and not in the bulk. Hence a sensitive balance has to be maintained for the plating (chemical reduction) to take place only on the surface. Even a slight change in the composition of the plating bath leads to instability which also causes homogeneous decomposition of the plating bath. To overcome this problem, small concentrations of additives are added to the bath. Schoenberg [1, 2] as well as Paunovic and Arndt [3] have revealed that additives may have two divergent effects: acceleration and inhibition. It can act as an accelerator or as a stabilizer. The stabilizers get adsorbed on the active nuclei and protect them from the reducing agent present in the plating solution. The deposition of the metal on the substrate itself can be completely prevented by adding stabilizers in excess. Accelerators are substances that boost the rate of plating. Generally, salts of organic acids serve as accelerators. The carboxylate ions present in organic acid adsorbs on the plating surface and catalyze the oxidation of formaldehyde and thus improves the plating rate. The rate of improvement in plating rate depends on the nature and concentration of the accelerator and also depends on the working condition of the plating process. Complexing agents play an important role in the process of electroless plating through chemical bath deposition [4]. Saturated polyhydroxylic alcohols emerge as a favorable alternative to EDTA. Saturated polyhydroxylic alcohols create exceptionally stable complexes with Cu(II) ions under alkaline conditions, thereby preventing the precipitation of $Cu(OH)_2$. Natural polyhydroxylic compounds are both eco-friendly and readily biodegradable, making them promising ligands for electroless copper baths. Among these, D-mannitol has been selected as a complexing agent for the current study, serving as an environmentally friendly alternative to EDTA for copper(II) ligands in electroless copper plating solutions.

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Copper is an excellent interconnect material in the present and future which finds application in high-end microprocessors and memory devices because of its less electrical resistivity and high electro migration resistance than other metals. Electroless copper coatings can even protect the metal surface which is exposed to corrosion and wear. Electroless copper plating possesses regular thickness throughout the substrate irrespective of shape, excellent conductivity, absorption, good adhesion and also provides excellent base for coatings [5, 6]. The major advantage of electroless plating is that it is carried out in the absence of electricity. This enables researcher's to carry out metallic plating on non-conductors like plastics (printed circuit board PCB), ceramics [7] and glasses [8] for decorative purposes. Fabrics find applications in electromagnetic interference (EMI) shielding and heat generators [9, 10]. In recent decades, the aggressive and highly toxic fluroboric acid and hydrofluoric acids is replaced with biodegradable green methane sulphonic acid (MSA). MSA possesses excellent metal salt solubility, higher conductivity, recyclability, i.e. recoverable from effluent and ease of effluent treatment [11]. The copper methane sulphonate possesses higher solubility than copper sulphate [12]. Hence the former is used for its above said properties and also for producing good quality deposits.

There are numerous patent literatures that primarily report on the influence of additives on the physical properties of electroless copper deposits [13, 14]. In electroless deposition organic and inorganic compounds can act as accelerators in traces (ppm). The addition of stabilizer is mandatory to overcome the sensitivity of the bath. This in turn decreases the deposition rate but get better deposits, i.e. fine grained deposits of copper with good adherence is observed. To improve the plating rate, accelerators are added. Additives that enhance the deposition rate to an acceptable level without causing instability to the plating bath are called as exaltants or accelerators. The present research aims to study the effect of guanidine hydrochloride and 2,6-diaminopyridine on electroless copper deposition by weight gain method, Tafel polarisation studies, surface morphological studies like SEM and XRD patterns for the deposits.

EXPERIMENTAL

In this study three different bath are compared viz bath A, bath B and bath C. The three different compositions of the bath are shown in Table.1. It consist of copper methane sulphonate salt as the metal source, D-mannitol is employed as an eco-friendly complexing agent, *p*-formaldehyde as a reducing agent, sodium hydroxide as pH adjustor, thiourea as stabilizers and guanidine hydrochloride and 2,6-diaminopyridine as accelerators. The above solution was prepared with high purity reagents and distilled water. The 99.99% pure copper substrates were used for plating process which required pre-treatment. The pretreatment was very essential in electroless deposition for uniform deposit and metal adherence to the substrate surface. The piece of the substrate 1 inch x 1 inch x 0.1 cm was cleaned with emery paper to remove oxide layer and treated with dil. H_2SO_4 to remove traces of oxide layer and washed thoroughly in deionised water. It was then activated in an acidic solution of 0.1 gL^{-1} $PdCl_2$. The substrate on washing with deionised water was dried and weighed. The weighed substrate is dipped in 100 mL of the plating bath solution for half an hour at room temperature (28 ± 0.2 °C). The deposition on the active site of the substrate begins with evolution of hydrogen gas. The formaldehyde got oxidized to formic acid with the liberation of hydrogen gas and at the same time cupric ion got reduced to copper on the catalytically active substrate surface. After the plating process the substrate was washed, rinsed with distilled water, dried and weighed to find the weight of the deposit. From the weight gain, the rate of deposition was calculated refer Table 1.

Tafel polarization measurements were studied by using an electrochemical analyzer of CHI 760C model. Tafel polarization measurements were experimented out in the plating bath containing three electrodes to recognize the effectiveness of the mixed potential theory in explaining electroless copper process.

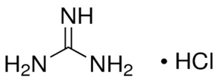
Table 1. Electroless copper plating bath composition

Bath constituents	Bath A	Bath B			Bath C		
Cu methane sulphonate	12.027 g/L	12.027 g/L			12.027 g/L		
D – Mannitol	13.5 g/L	13.5 g/L			13.5 g/L		
p-Formaldehyde	10 g/L	10 g/L			10 g/L		
pH	13. 0-13.3	13. 0-13.3			13. 0-13.3		
Temperature	28 ±0.5 °C	28 ±0.5 °C			28 ±0.5 °C		
Thiourea	0.1 ppm	0.1 ppm			0.1 ppm		
Accelerators		Guanidine hydrochloride			2,6-Diaminopyridine		
Concentration		0.001 M	0.01 M	0.05 M	0.001 M	0.01 M	0.05 M
Plating rate = Wx10^4/DAT (μm/h)	2.3	2.4	2.6	2.8	3.7	4.1	4.5

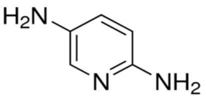
In the three-electrode set up, copper electrode of 1 cm^2 area acts as the working electrode, reference electrode would be standard calomel electrode and platinum electrode acts as the counter electrode. The electrodes were polarized anodically and cathodically 10 mV/s from their open circuit potential (OCP). Tafel investigation was carried out for bath A (no accelerator), B and C with a concentration of 0.05 M of guanidine hydrochloride and 2,6-diaminopyridine, respectively, at room temperature of 28±0.5 °C.

The X-ray diffraction patterns obtained were verified by X'pert pro-XRD, (make-P analytical, USA) instrument to investigate the deposits. To determine the grain size of the electroless deposits, it was examined using a SEM with an acceleration voltage range of 20,000 V by using the S-3000 model and with the magnification range of x1000 and x2500.

Structure of accelerators:



Structure of guanidine hydrochloride



Structure of 2,6-diaminopyridine

RESULTS AND DISCUSSION

Weight gain method

The deposition rate in the presence and absence of accelerators for three different concentrations (0.001, 0.01, and 0.05 M) are shown in Figure.1.

Guanidine hydrochloride accelerates electroless copper solution by increasing the deposition rate as the concentration is increased [15]. 2,6-Diamino pyridine shows a higher rate of acceleration and deposition rate from 3.7 to 4.5 µm/h. This is because the molecular framework of 2,6-diaminopyridine includes a benzene ring that aids in facilitating pi electron interactions. Additionally, the presence of nitrogen atoms at the 2nd and 6th positions in the pyridine compound promotes facile adsorption, thereby enhancing the oxidation of p-formaldehyde. The presence of 2,6-diaminopyridine not only accelerates the plating rate but also improves the stability of the bath [16].

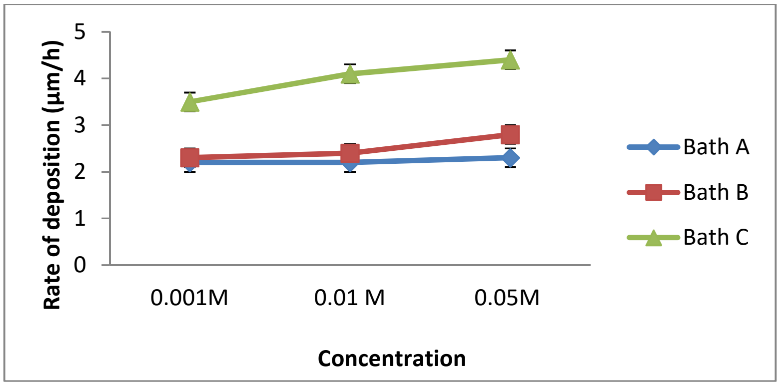


Figure.1. Rate of deposition of accelerators at 0.001, 0.01 and 0.05 M concentration.

Tafel polarization studies

Electroless plating is mainly explained by mixed potential theory which is a combination of both the electrochemical reactions taking place simultaneously. In the present study, Tafel polarization was used to determine the mechanism of effect of acceleration on deposition rate by i_{dp} (deposition current) and E_{dp} (deposition potential) as mixed potential [17, 18]. In tafel polarization tangent were drawn on anodic and cathodic curves to determine the i_{dp} and E_{dp}. Slopes were drawn to identify the b_c (cathodic) and b_a (anodic) slope values, The rate of deposition from ASTM standard [17] is given as follows:

$$\text{Deposition rate } (\mu\text{m/h}) \;=\; 3.7328 \text{ x } 10^{-4}\,(i_{dp}/\rho)\text{ Eq. wt}$$

For copper metal deposition the above equation reduces as

$$\text{Deposition rate } (\mu\text{m/h}) \;=\; 1.363 \text{ x } 10^{-3}\,(i_{dp}\,)$$

It is very clear from Table 2 that the deposition current i_{dp} for guanidine hydrochloride (bath B, 0.05 M) as well 2,6-diaminopyridine (bath C, 0.05 M) possess higher current than the bath A indicating their acceleration property which well correlates with the trend of weight gain method. The Tafel polarization curve of bath A, bath B and bath C is shown in Figure 2. The deposition rate values are not same due to limitation associated with mixed potential theory [19]. The acceleration property is due to two reasons: adsorption on the active surface and enabling oxidation of formaldehyde and depolarizing the surface which enhances easy reduction of cupric ion to copper on the substrate [20]. The adsorption is due to the electrons on hetero atom in guanidine hydrochloride three N atom and also a pair of pi electron. In 2,6-diamino pyridine aromatic ring provides pi-electron cloud and also possess three N atom making it more effective in acceleration than guanidine hydrochloride [21]. i_{dp} is greater for bath B and C indicating that it enhances the reaction, anodic Tafel polarization b_a value also increases appreciably indicating acceleration of anodic reaction [22].

Table 2. Tafel polarization study for electroless copper deposition – D-mannitol bath with and without accelerators.

S. No.	Accelerator	b_a mV/decade	b_c mV/decade	i_{dp} mA	E_{dp} mV	Deposition rate µm/h
1	Bath A	80.8	- 415	320.4	-783.6	0.437
2.	Bath B (0.05 M)	84.4	-479.8	327.3	-636.7	0.446
3.	Bath C (0.05 M)	92.7	-549	335.8	-683	0.458

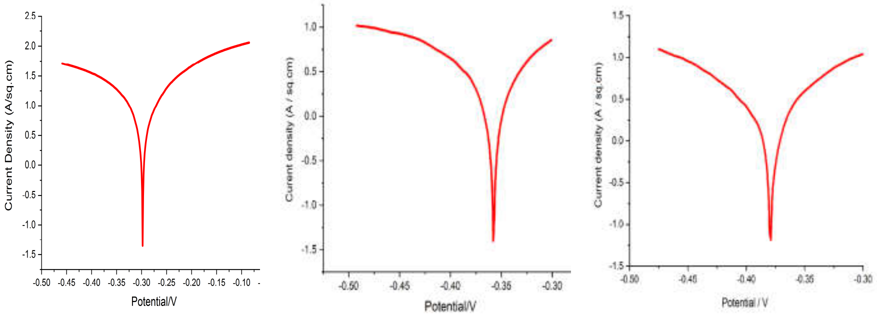


Figure 2. Tafel polarization curve of a) bath A, b) bath B and c) bath C with scan rate of 10 mV/s, at pH 13.3 (28±2 ºC).

X-Ray diffraction studies (XRD)

The X-ray diffraction studies play a vital role in studying the crystal orientations and the lattice parameters of the copper deposits. All the (hkl) peaks of the pure copper metal indicate only preferred orientation of (111) plane. According to Junginger *et al.* [23] that the preferred orientation was given 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 preferred orientation was (111) plane having lowest surface free energy, which was so far standard for copper film. Braggs diffraction peaks at 2θ shows peaks corresponding to (111), (200), (220) and (311) crystal planes at 43.3°, 50.5°, 74.1° and 89.9° confirms the presence of copper crystals and not CuO according to JCPDS File No. 0040836. The predominant preferred orientation of 200 plane for all the three baths is shown in Figure 3, which has been already reported from previous work [24, 25]. This may be due to the methane sulphonate ion influencing the orientation of copper atom [26]. The copper deposit's crystallite size was estimated by employing Scherrer's equation [27, 28], which is provided below:

$$D_{hkl} = \frac{k\lambda}{\beta \cos\theta}$$

The crystallite size of bath A, B and C are almost closer and shows nano scale dimension 42.45 nm, 37.41 nm and 41.66 nm from Table 3. The additive guanidine hydrochloride and diphenylamine has very less impact on crystallite size.

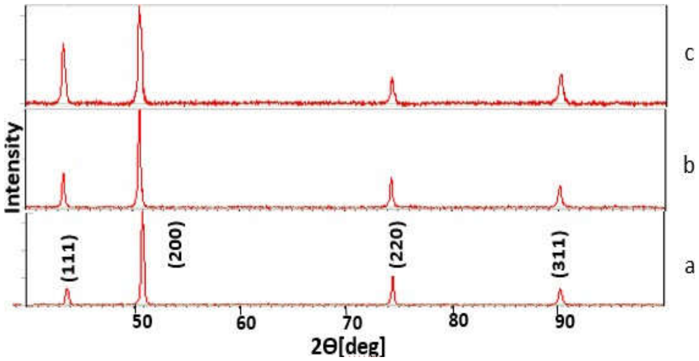


Figure 3. XRD graph of copper deposition electrolessly in a) bath A, b) bath B and c) bath C.

Table 3. Crystallite size of copper deposit of accelerators with D-mannitol as complexing agent.

S. No.	Accelerators	Crystallite size (nm)
1	Bath A	42.45
2	Bath B (0.05 M)	37.41
3	Bath C (0.05 M)	41.66

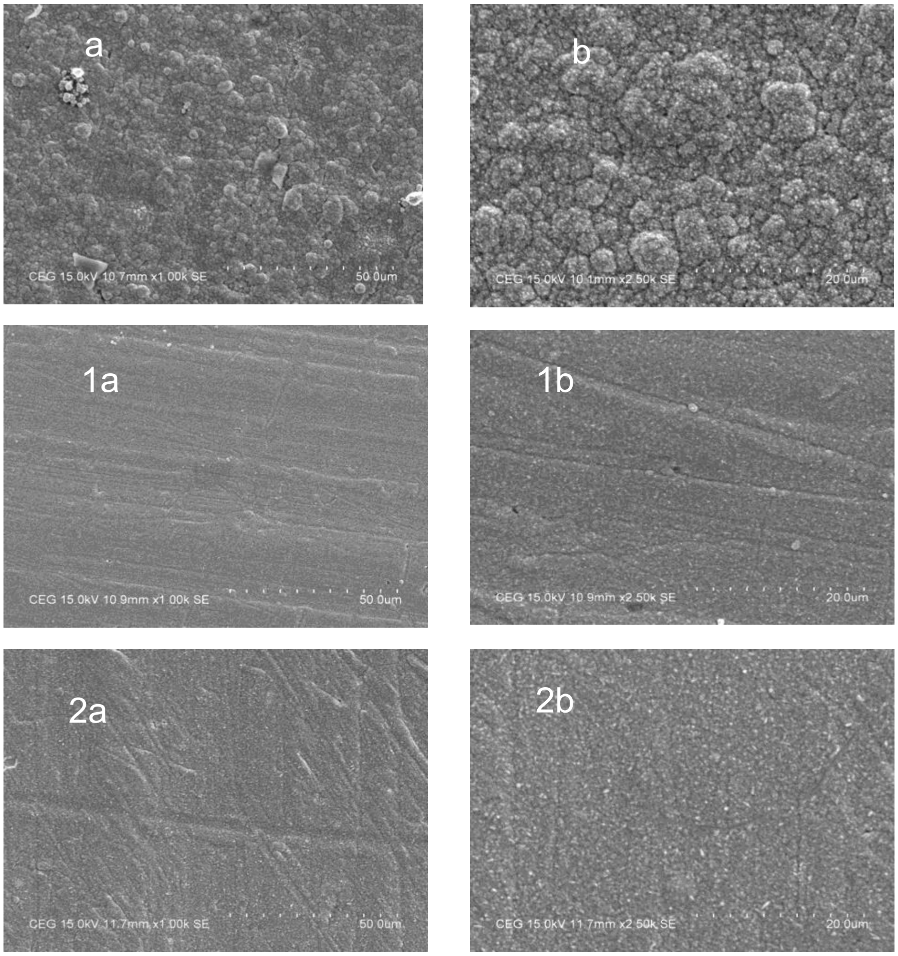


Figure 4. SEM photograph of electrolessly deposited copper in bath A a) x 1000, and b) x 2500, bath B 1a) x 1000 and 1b) x 2500, bath and C 2a) x 1000 2b) x 2500.

Scanning electron microscopic analysis

The SEM analysis shows the two-dimensional structure of the copper deposits. The SEM analysis of copper deposits was studied at a magnification of × 1000 and × 2500 of bath A, B and C. It was observed that bath B and C showed very fine and smooth deposits than the deposits from bath A. Bath A showed a nodular deposit which was clearly visible from grains in Figure 4b which were very clear in 2500 magnification. Bath B and C gave a very fine and smooth deposition 1000 magnification photo and upon 2500 magnification deposit are fine grained with nodular shape. This was indicating that guanidine hydrochloride and 2,6-diamino pyridine regulates the deposition process, pore free fine deposits were observed. The fine grained deposits of guanidine hydrochloride and 2,6-diamino pyridine was accounted for more number of nucleation on the surface, as they accelerated the reaction.

CONCLUSION

Additives show an important role in maintaining the bath stability of the electroless copper. In this present study the following findings were observed: (1) The accelerator enhanced the deposition rate by maintaining the bath stability in the presence of 0.1 ppm of TU. (2) Among the accelerators used, the accelerating effect of guanidine hydrochloride was found to be lower than that of 2,6-diaminopyridine. (3) Tafel polarization studies results correlated well with the weight gain studies confirming their effects on plating rate as well as stability. (4) The preferred orientation for the deposited copper is (200) plane with high intensity and the crystallite size was found to be in nano scale for both the accelerators employed. (5) The SEM analysis for deposited copper specimen for D-mannitol bath was found to be very smooth and fine deposits even with x2500 magnification. 2,6-Diaminopyridine showed a good pore free surface coverage with D-Mannitol bath with excellent rate of deposition. (6) When compared with plain bath accelerators used in this study enhance the rate of plating due to the presence of delocalized π - electrons. Tafel polarization studies also confirmed the accelerating behaviour of the additives used which is also confirmed by XRDand SEM analysis.

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