RJC

RASĀYAN *J. Chem.*
Vol. 15 | No. 2 |1154-1159| April - June | 2022
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

INVESTIGATION OF ENHANCING THE PERFORMANCE AND DEPOSITION CHARACTERISTICS OF COPPER (II) METHANE SULPHONATE SALT COMPLEXED WITH D-MANNITOL BATH

S. Jothilakshmi[1], S. Rekha[2,✉], A. Alvin Kalicharan[3] and R. Ranjani[4]
[1]Department of Chemistry, RMK College of Engineering and Technology, Puduvoyal-601206, (TamilNadu) India
[2]Department of Chemistry, RMD Engineering College, Kavaraipettai-601206, Tamil Nadu, India
[3]Department of Chemistry, Panimalar Engineering College, Chennai-600123, Tamil Nadu, India
[4]Department of Physics, RMD Engineering College, Kavaraipettai-601206, Tamil Nadu, India
✉Corresponding Author: rekhaperichiappan@gmail.com

ABSTRACT
The performance of the eco-friendly D-Mannitol electroless copper plating bath with additives has been investigated. D-Mannitol produces a lower plating rate which has been improved using exaltants viz., polyethylene glycol 600, oxalic acid and malonic acid. The performance of the bath shows improvement gravimetrically and by polarization studies. The surface morphology studies are also interpreted.
Keywords: Eco-friendly, D-Mannitol, Additives, Copper plating, Impedance, Tafel polarization.
RASĀYAN *J. Chem*., Vol.15, No.2, 2022

INTRODUCTION

In 1946, the origin of electroless plating was invented by Brenner and Riddell[1] with electroless nickel plating. In the immediate future in 1950 electroless copper was identified to develop solutions for plating plated through-hole (PTH) and printed wiring boards (PWB). In recent years electroless plating is carried out on fabrics for electromagnetic interference shielding[2] and the metals like silver, copper[3] posses the antibacterial, antiseptic and antiviral properties. The electroless copper plating baths developed earlier was subjected to spontaneous decomposition. Continual advancement has taken place in the controlling factors and continued to be confirmed in a wide range of studies.[4,5]

Extensive research has been carried out employing complexing agents like EDTA[6] (Ethylenediaminetetraacetic acid), sodium tartrate[7], glycerine[8], Triethanolamine[9], and ammonia.[10] EDTA is an exceptional chelating agent which forms a metal-EDTA complex at a higher pH range and prevents $Cu(OH)_2$ precipitation.[6,11] Even though EDTA complexes well, it forms a stable heavy metal complex that accumulates in the environment being non-biodegradable and also enhances the nitrogen content totally in the wastewater.[12,13] To overcome the above drawbacks saturated polyhydric alcohols which are easily biodegradable and eco-friendly were tried as an alternative.

Saturated polyhydric alcohols[14-16] form a very stable complex with Cu(II) ions which in turn prevent the precipitation of $Cu(OH)_2$ at pH greater than 12. In the development of eco-friendly baths, copper methane sulphonate salt has been found to be a better choice of salt for electroless copper deposition.[17] Additives are excellent surface-active compounds that produce a variety of effects for the metallization process.[18] Additives can be classified as stabilizers or accelerators. Stabilizers improve the bath stability while accelerators enhance the deposition rate.

The present investigation focuses to study the effect of D-Mannitol as a complexing agent and accelerators like polyethylene glycol 600 (PEG600), oxalic acid, and malonic acid on an electroless copper deposition by weight gain method and polarization technique. The deposit's surface morphology was well understood by XRD and SEM analysis.

EXPERIMENTAL

The plating process was carried out for 1h at room temperature (28±0.5°C) with the plating bath containing: 12g/l of copper methane sulphonate as a metal salt, 13.5g/l of D-Mannitol as a complexing agent, 10g/l of p-formaldehyde as reducing agent at a pH of 13.3, Sodium hydroxide (NaOH) is used to adjust the pH and stabilizer, 0.1 ppm of thiourea to ensure stability. The copper substrate of area 2.5 x 2.5 x 0.2 cm^3 was degreased; oxide removed and activated in acidic $PdCl_2$ for the 30s on both sides. The substrate is then cleaned with double distilled water, well dried, weighed, and dipped in the 100ml plating solution for deposition. The evolution of hydrogen bubbles from the plating surface confirms the start of the plating process.

Detection Method

The deposition rate of copper was determined by the gravimetric method. The measurements were repeated at least twice for accuracy. Polarization studies like cyclic voltammetric studies, Tafel polarization measurements, and impedance studies were obtained by using the standard electrochemical analyzer CHI 760C. The above studies were carried out in the plating bath with three electrodes set up consisting of the copper electrode of 1cm^2 area as the working electrode, a standard calomel electrode as a reference electrode, and a platinum electrode as the counter electrode. The electrodes were polarized anodically and cathodically with a scan rate of 10mV/s from their open circuit potential. The structural properties such as crystallite size and the quality of the deposited copper substrate were analyzed by X-ray diffraction pattern (Xpert pro, p-analytical). The morphology of the copper surface was evaluated using a Scanning electron microscope (S-3000) with an accelerating voltage of 20 kV and with a magnification of x2500.

RESULTS AND DISCUSSION

Weight Gain Method

The pretreated copper substrate is weighed before and after the electroless deposition process. From the difference in weight, the deposition rate is determined. It is found that the D-Mannitol plain bath containing 0.1ppm of Thiourea as stabilizers, showed a deposition rate of 2.0µm/h. The weight gain studies were carried out with accelerators (PEG600, oxalic acid, and malonic acid) for three different concentrations of 0.001M, 0.01M, and 0.05M tabulated in Table-1. From Table-1, PEG 600 showed an increasing plating rate with increasing concentration. The deposits obtained with PEG 600 were semi-bright in color. Malonic acid and oxalic acid showed an increasing performance with an increase in the concentration confirming the accelerating property. The deposits obtained were dark in color and well adhered to the substrate. Oxalic acid showed a higher influence on the plating rate.

Table-1: Effect of Accelerators on Deposition Rate in D-Mannitol Optimized Bath with 0.1ppm Thiourea at Three Concentrations of 0.001M, 0.01M and 0.05 M

	Rate of deposition(µm/h) = $\frac{W \times 10^4}{DAt}$		
Plain bath	2.0		
Accelerators	Concentration		
	0.001 M	0.01 M	0.05 M
PEG 600	2.4	2.6	2.9
Malonic acid	2.4	2.8	3.2
Oxalic acid	2.6	3.0	3.4

Tafel Polarization Studies

In electroless copper plating, the reduction of copper ion and formaldehyde oxidation occurs simultaneously at the surface of the metal at mixed potential (E_{mp}) more precisely to be the deposition potential (E_{dp}) and i_p deposition current. The rate of deposition is calculated as per ASTM (American Society for Testing and Materials) standard[19] with the following equation,

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

The i_{dp} value for the accelerators studied is found to be greater than plain bath as shown in Table-2, which entails the acceleration of the plating process. The acceleration behavior of the additives is due to their adsorption on the catalytically active surface, which enhances the oxidation of formaldehyde producing

electrons at a faster rate. The produced electron increases the rate of reduction of cupric ion to copper on the substrate surface.[20] The Tafel graphs for the plain bath and the bath containing accelerators are shown in Fig-1. Deposition rates calculated from the i_{dp} value are lesser than that calculated from the gravimetric method due to the limitation related to mixed potential theory.[19] The effects on the deposition rate of different accelerators are similar to the gravimetric method.[21]

Table-2: i_{dp} values and Deposition Rate for the Tafel Polarization Studies, Formaldehyde Oxidation Current for Cyclic Voltammetric Studies, R_{ct} and C_{dl} Values for Impedance Studies, and Crystalline Size for XRD Patterns of The Accelerators Employed In D-Mannitol Bath.

S.no	Accelerators	Tafel		CV	Impedance		XRD
		i_{dp}	Deposition rate	Peak current of Formaldehyde oxidation (mA/cm^2)	R_{ct}(ohm/cm^2)	C_{dl}x10^{-5}(F/cm^2)	Crystallite size (nm)
1.	Plain bath	295.1	0.4022	7.85	8.22	6.96	42.45
2.	PEG 600	312.3	0.4256	8.23	7.659	8.158	41.66
3.	Malonic acid	329.8	0.4495	8.49	4.816	8.254	40.46
4.	Oxalic acid	370.5	0.5049	8.87	4.231	8.435	39.28

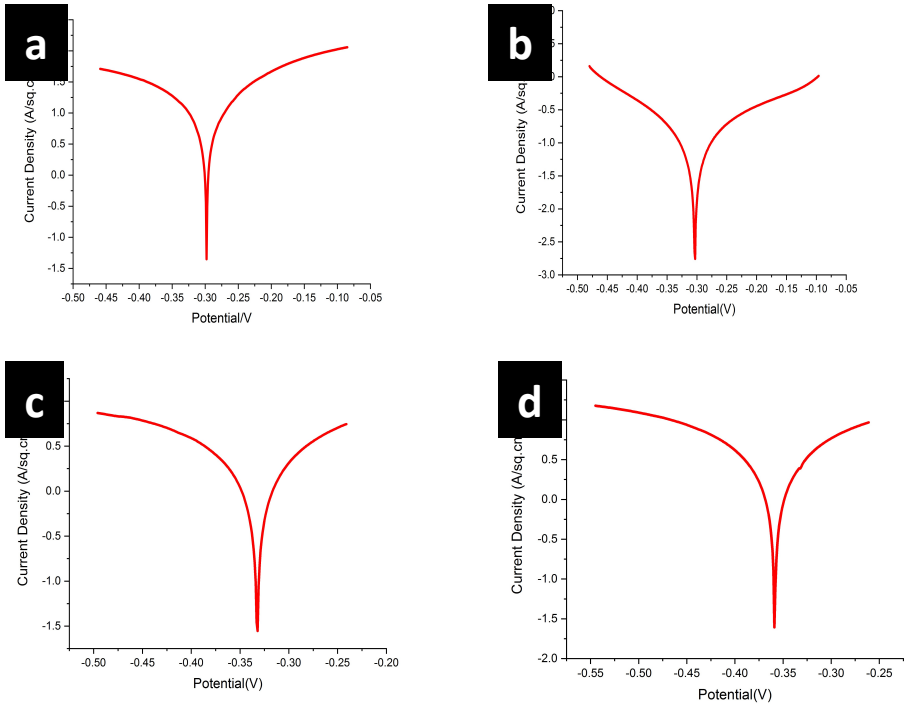

Fig.-1: Tafel Polarization Curves of D-Mannitol bath; Scan Rate 0.01V/s, pH 13.3 at Room Temperature (28±0.5ºC) With a. Plain Bath b. PEG600 c. Malonic Acid d. Oxalic Acid at 0.05M Concentration

Cyclic Voltammetric Studies

The plain bath and accelerator baths were subjected to cyclic voltammetric studies and the graphs are shown in Fig.-2 and the i_{dp} and deposition values are shown in Table-2. The oxidation peak current value of PEG 600 is slightly elevated than the plain bath, indicating that PEG 600 accelerates the electroless copper bath. The adsorption on the surface occurs at the oxygen atom possessing lone pair of electrons and also by speeding up the oxidation process.[22] The oxidation peak current value of malonic acid and oxalic acid is higher than plain bath is accounted to the presence of COO^- group[23] in the additives, which helps in adsorption on the plating surface. The oxalic acid being more compact than malonic acid, more molecules gets adsorbed on the surface and also enhances the oxidation process to a greater extent than the malonic acid, which has one additional methyl group in its structure.[20]

Impedance Studies

For the present plating bath, the double-layer capacitance (C_{dl}) and the charge transfer resistance (R_{ct}) were calculated by employing the Nyquist plot.[24,25] The Nyquist plot is widely known as impedance spectrum, which is an accepted format to plot graphs between Z" (imaginary component) and Z' (real component) at measured frequency. The electroless copper plating containing accelerators showed plots with high-frequency capacitive features.

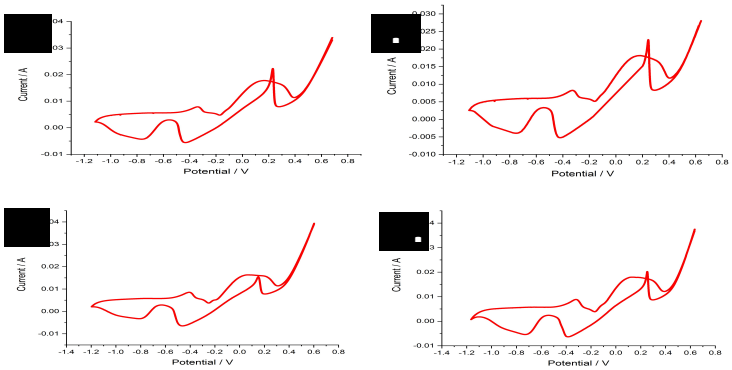

Fig.-2: Cyclic Voltammogram of D-Mannitol Bath with a. Plain Bath b. PEG600 c. Malonic Acid d. Oxalic Acid(0.05 M) at pH 13.3

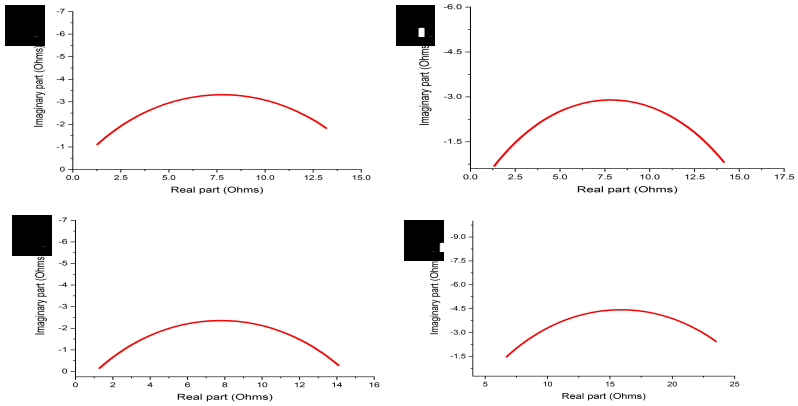

Fig.-3: Nyquist Diagram of D-Mannitol Bath with a. Plain Bath b. PEG600 c. Malonic Acid d. Oxalic Acid (0.05 M) at pH 13.3.

This is mainly caused due to the complexation of the accelerator with Cu(I) ion[26] and adsorption of the accelerator on the surface of the electrode exhibit the inhibition of the electrode reaction by the additives. The R_{ct} and C_{dl} values are tabulated in Table-2 and the impedance graphs are shown in Fig.-3. The charge transfer resistance values (R_{ct}) is found to be lesser than the plain bath and double layer capacitance (C_{dl}) values greater than the plain bath, confirming the acceleration in the plating rate. Among the accelerators used oxalic acid possesses the least R_{ct} value signifying improved accelerating property as the resistance of the solution is decreased and helps the oxidation and reduction reactions.

X-Ray Diffraction Studies (XRD)

The XRD patterns for various plating baths are shown in Fig.-4. The diffraction peaks observed in this present study are (111), (200), (220) and (311). All the four baths showed (200) planes with high intensity due to the presence of methane sulphonic acid[27,28] in the bath. By using Scherrer's equation[29] crystallite size of the deposited copper was calculated for the diffraction peak of the (200) plane. The crystallite size ranges from 39 to 42.45 nm (Table-2). Thus D-Mannitol bath produces nano crystallite size for all the accelerators under study as well as for the plain bath.

Scanning Electron Microscope Analysis (SEM)

The SEM images for D-Mannitol plain bath and the bath containing accelerators are shown in Fig.-5. The plain bath and accelerators viz. PEG 600 and malonic acid showed pore-free smooth deposits (Fig.-5a to c). The morphology of the surface in the presence of oxalic acid showed smooth wave-like deposits (Fig.-5d).

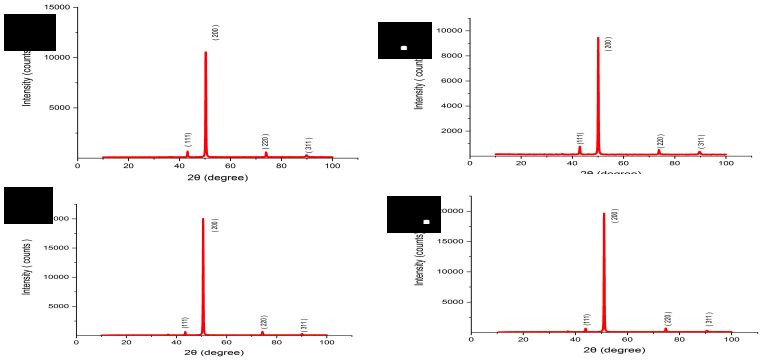

Fig.-4: XRD Patterns of Copper Deposits of D - Mannitol Bath a. Plain Bath b. PEG600 c. Malonic Acid d. Oxalic Acid (0.05 M).

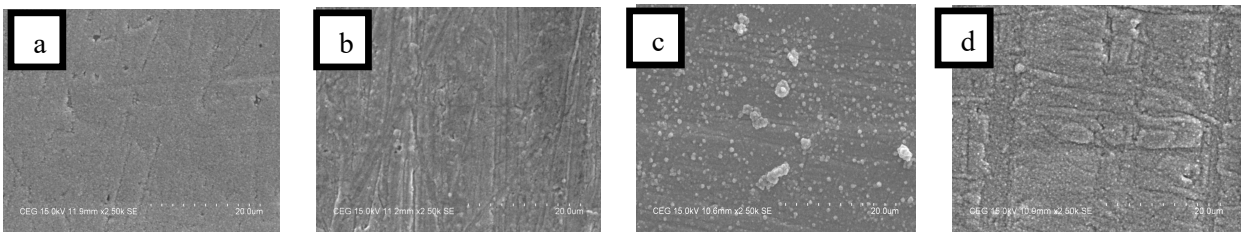

Fig.-5: SEM Photograph of Electrolessly Deposited Copper with a. Plain Bath b. PEG600 c. Malonic Acid d. Oxalic Acid (0.05 M) at x 2500 Magnification

CONCLUSION

The present investigation has proved that the eco-friendly electroless copper bath with D-Mannitol complexant for copper methane sulphonate salt showed a promising future with the addition of accelerators. The additives PEG600, oxalic acid, and malonic acid improved the deposition rate significantly. The electrochemical studies Tafel, cyclic voltammetric studies, and impedance method also confirmed the enhanced deposition rate of the plating bath. The SEM analysis showed that the deposits obtained were smooth, pore-free, and fine-grained.

REFERENCES

1. A. Brenner and G. E. Riddell, *Journal of Research of the National Bureau of Standards*, **37**, 31 (1946), http://dx.doi.org/10.6028/jres.037.019
2. Azam Ali, Vijay Baheti, Michal Vik, Jiri Militky, *Journal of Physics and Chemistry of Solids*,**137**,109181(2020), https://doi.org/10.1016/j.jpcs.2019.109181
3. M.S. Sataev, Sh.T. Koshkarbaeva, K.B. Amanbaeva, P.A. Abdurazova, G.T.Assilbekova, Y.B. Raiymbekov and D.Urazkeldieva, *Rasayan Journal of Chemistry,* **15(1)**, 31(2022), http://dx.doi.org/10.31788/RJC.2022.1516595
4. Cheryl A. Deckert, *Plating & Surface Finishing*, **82**, 48(1995).
5. S. Dheenadhayalan , V. Nijarubini and J. Mallika, *Rasayan Journal of Chemistry*, **11(2)**, 634(2018), http://dx.doi.org/10.31788/RJC.2018.1122085
6. L.G. Sillen and A.E. Martell (Eds), *Stability Constants of Metal- Ion Complexes*, Special Publication No 25, Supplement No 1, Chemical Society, London, 1964, https://doi.org/10.1007/978-1-4899-1486-6-7
7. Rolf Aschenbrenner, Andreas Ostmann, Ute Beutler, Jurgen Simon and H. Reichl, *IEEE Transactions on Components, Packaging and Manufacturing Technology-Part B*, **18**, 334(1995), http://dx.doi.org/10.1109/96.386270

8. H. Koyano, *Journal of the Electrochemical Society*, **139(11)**, 3112(1992), https://doi.org/10.1149/1.2069041
9. K. Kondo, J. Ishikawa, O. Takenaka and T. Matsubara, *Journal of the Electrochemical Society*, **138 (12)**, 3629(1991), https://doi.org/10.1149/1.2085470
10. F.Z. Sadafi, C. Sauerbeck, B. Braunschweig, and R.N. Klupp Taylor, *CrystEngComm*, **20**, 6214(2018), https://doi.org/10.1039/C8CE00866C
11. E. Hogfeld, *Stability Constants of Metal-Ion Complexes. Part A: Inorganic Ligands*, Pergamon Press, Oxford, 1982.
12. M.D. Tucker, L.L. Barton, B.M. Thompson, B.M. Wagener and A. Aragon, *Waste Management*, **19 (7-8)**, 477(1999), https://doi.org/10.1016/S0956-053X(99)00235-4
13. M. Sillanpa, V. Vickackaite, L. Niinisto, M.L. Sihvonen, *Chemosphere*, **35(12)**, 2797(1997), https://doi.org/10.1016/S0045-6535(97)00278-6
14. K. Hegetschweiler, *Chemical Society Reviews*, **28(4)**, 239(1999), https://doi.org/10.1039/A802638F
15. K. Burger, L.Nagy, K. Burger , *Bio Coordination Chemistry: Coordination Equilibria in Biologically Active Systems*, Elis Hoorwood, Chichester, 1990, https://doi.org/10.1016/0162-0134(92)80009-k
16. J.F. Verchere; S. Chapelle; F. Xin and D.C. Crans, in K.D. Karlin , *Progress in Inorganic Chemistry*, John Wiley & Sons, New York, **47**, 837(1998).
17. Frank C.Walsh, *Surface & Coatings Technology*, **259**, 676(2014), https://doi.org/10.1016/j.surfcoat.2014.10.010
18. L.Sue-Hong, S. Jia-Min, C.Chih, H. Karl and C.Shih-Song, *Journal of the Electrochemical Society*, **153(6)**, C428(2006), https://doi.org/10.1149/1.2193348
19. ASTM G102, *Standard practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements* (1994)**.**
20. Thomas M. Tam, *Journal of the Electrochemical Society*, **132(4)**, 806(1985**)**, https://doi.org/10.1149/1.2113962
21. ASTM-G3- 89, *Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing* (2004).
22. R. Z. Acosta, T. L. Romankin, *Abstract 277*, 736, 77- 2, Atlanta, Georgia, October 9-14 (1997).
23. R. Tarozaitė; A. Selskis, *Transactions of the Institute of Metal Finishing,* **84**, 105(2006).
24. Sebastian Feliu, *Metals*, **10(6)**, 775(2020), https://doi.org/10.3390/met10060775
25. Lasia.A, *Electrochemical Impedance Spectroscopy and its Applications-Modern Aspects of Electrochemistry*, White, R.E., Conway, B.E., and Bockris, J.O.M., Eds., Plenum Press, New York, 143 (1999).
26. J.R. MacDonald, *Impedance Spectroscopy*, John Wiley &Sons, New York, NY, (1987).
27. AnithaVigneswaran, VenkateshPerumal, *AutAut Research Journal*, **11(4)**, 277(2020), https://doi.org/10.0001865.Aut Aut.2020.V11I4.463782.00553
28. S.Absara Fdo, P.Venkatesh, P.Balaramesh, *Materials Today Proceedings*, **47**, 9(2021) https://doi.org/10.1016/j.matpr.2021.03.583
29. Ogundare.O. D; Akinribide.O. J; Adetunji.A. R; Adeoye.M. O; Olubambi.P. *Procedia Manufacturing,* **30**, 173(2019).

[RJC-6837/2021]