

Electroless deposition of copper from methane sulphonate complexed bath

S. Rekha¹, K. N. Srinivasan*² and S. John²

Electroless copper deposition is widely used for printed circuit applications. A new bath based on copper methane sulphonate replacing copper sulphate, EDTA and paraformaldehyde has been developed, which is very useful for plating on non-conductors and through hole plating in printed circuit manufacturing processes. The new bath has a higher rate of deposition of $3.3 \mu\text{m h}^{-1}$ than the conventional sulphate bath (with a rate of $1.5 \mu\text{m h}^{-1}$) and the bath stability and the quality of the deposits are very good. Scanning electron microscopy, X-ray diffraction and atomic force microscopy studies have been carried out and the crystallite size of the copper is measured to be 134 nm with a preferred orientation of 200 planes. The deposit obtained is pure copper and the surface roughness is of the order of 10 nm.

Keywords: Electroless copper, Methane sulphonate, Chemical deposition, Paraformaldehyde, PCB industries

Introduction

The growth of the electronics industry and the arrival of the printed circuit board (PCB) bestowed a great deal of importance on the metal copper, and the need arose to devise satisfactory means by which it could be electrolessly deposited. When the problem of interconnecting both sides of a printed circuit arose, the first approach was by mechanical means, such as riveting or eyeletting. As the technology of PCBs advanced, requirements necessitated the need for more holes per unit area in the board. As the mechanical method of interconnections was costly, attention was turned to electroless deposition techniques. Copper was chosen for deposition because of its high conductivity, excellent solderability and possibility of deposition at room temperature. The result was that many electronic companies started research programmes to obtain workable solutions, as most of the available processes were seen as out dated, unstable and completely unsuitable. The basis of these solutions was two discoveries made in the nineteenth century. In 1856, Liebig suggested the use of solutions of silver nitrates and glucose for mirror manufacture, replacing amalgam coatings, which were poorly reflecting.¹ Currently, formaldehyde is used for the reduction of silver. This reducing agent was not available at Liebig's time. Formaldehyde was discovered by Liebig's student Hofmann as an oxidation product of CH_3OH .²

In 1850, Fehling found that divalent copper could be reduced as copper (I) oxide when an aldehyde (or sugar) reacts with copper tartrate complex in hot alkaline

solution. The so called Fehling's solution gained importance in medical chemistry for the indication of sugar in the urine of diabetics. Chattaway attempted in 1907 to copper plate on glass in a solution containing copper and formaldehyde.³⁻⁸ Goldie,⁴ Lowheim⁵ and Saubestre⁶ reported the state of development up to 1965. Most of the solutions used today are based on a modified Fehling's solution, normally referred to as the Fehling, i.e. formaldehyde based bath consisting of CuSO_4 (source of metal ion), NaOH (pH adjuster), formaldehyde (reducing agent) and sodium potassium tartrate (complexing agent). Many attempts were made to increase the rate of deposition and stability of the bath by the proper choice of bath constituents.⁷⁻¹⁰

A literature survey indicates that very little work has been conducted on the electroless deposition of copper methane sulphonate (metal salt). Methane sulphonate acid (MSA) has gained popularity in electroplating related to electronic industries¹¹⁻¹³ in the past two decades. It has been successfully used as a complexant for Cu-Sn ¹⁴⁻¹⁶ and Sn ¹⁷ plating baths. It also finds its application in electrorefining of Pb ¹⁸ and electroplating of metals, such as Ag ,¹⁹ Ni ²⁰ and Cu .²¹ In copper electroplating, it is observed that copper deposition occurs at much lower over potential and high rate of grain nucleation²² and also it is used in metallisation²³ of micrometre or submicrometre dimensioned trenches or vias. Moreover, MSA^{24,25} is characterised by excellent metal salt solubility, excellent conductivity and ease of effluent treatment, bath stability, low toxicity and biodegradability. Further replenishment²⁶ of the solutions requires only a small volume of copper methane sulphonate. The small replenishment volume maintains a constant operating temperature that in turn produces uniform and high quality coatings. Conventionally formaldehyde is the reducing agent widely used for electroless copper deposition.

¹RMD Engineering College, RSM Nagar, Kavaraipeitai, Chennai 601206, Tamil Nadu, India

²Central Electrochemical Research Institute, Karaikudi 630006, Tamil Nadu, India

*Corresponding author, email knsvasan@gmail.com

The present work aims to study the formation and characterisation of electroless copper deposits using copper methane sulphonate as a source of metal ions.

Experimental

Preparation of stock solution

About 100 g of copper carbonate was weighed and transferred in a 1 L clean beaker and treated with a minimum quantity of MSA (~120 mL) until effervescence ceased. A minimum quantity of double distilled water was added for easy evolution of carbon dioxide gas. The solution was made up to the 500 mL mark with double distilled water. The oils and suspended impurities present in the solution were removed by filtration. The solution was stored in a clean closed container. The copper methane sulphonate stock solution $\text{Cu}(\text{CH}_3\text{SO}_3)_2$ was analysed for the Cu^{2+} ions concentration using EDTA titration.

Preparation of copper specimens

Copper specimens of 99.99% purity of size $2.5 \times 2.5 \times 0.2$ cm were polished with fine grit papers, degreased and rinsed in double distilled water. Then the specimens were cathodically alkaline cleaned in the following solution for 5 min at a current density of 3 A dm^{-2} at a bath temperature of $28 \pm 2^\circ\text{C}$:

- (i) sodium metasilicate (45 g L^{-1})
- (ii) trisodium phosphate (45 g L^{-1})
- (iii) wetting agent (1.5 g L^{-1})
- (iv) sodium carbonate (15 g L^{-1}).

After alkaline cleaning, the copper panels were washed well with tap water, followed by distilled water and then dipped in 10% sulphuric acid. They were again washed with tap water, rinsed in double distilled water and dried. The initial weight of the test panel was recorded. Then the panels were activated in a solution of 0.1 g L^{-1} $\text{PdCl}_2 + 50 \text{ mL}$ of HCl for 30 s. After activation, the specimens were rinsed well and then subjected to electroless plating in a 100 mL bath. In most of the cases, initiation was complete in 0.5–1 min. No agitation was provided during the plating and the experiments were carried out for 30 min at room temperature. Upon deposition the panel was removed and washed with double distilled water and dried. The final weight of the panel was taken and the difference in weight gives weight of deposit. A single pan digital balance with 0.1 mg accuracy was used for mass measurements to determine the rate of deposition through weight gain. Each experiment was repeated twice to get reproducible results. The rate of deposition was calculated using the following formula

The rate of deposition ($\mu\text{m h}^{-1}$) = $W \times 10^4 / DTA$ (1)

where W is the weight of the deposit (g), D is the density of

Table 1 Effect of copper ion concentration on rate of deposition and bath stability

Concentration of copper/ g L^{-1}	Rate of deposition/ $\mu\text{m h}^{-1}$	Stability of bath
1	0.8	Stable
2	2.6	Stable
3	3.3	Stable
4	5.9	Moderate stability
5	8.0	Unstable

the deposit (g cm^{-3}), T is the plating duration (h) and A is the surface area of the specimen (cm^2).

A digital pH meter (Elico, Hyderabad, India) was used to measure the pH of the various plating baths and electrolytes. All the chemicals used were of analytical or guaranteed reagent grades.

The selected bath composition and its operating conditions, after preliminary experiments on plating rate and bath stability, are given below.

Bath composition:

- (i) copper as methane sulphonate (3 g L^{-1})
- (ii) disodium salt EDTA (20 g L^{-1})
- (iii) paraformaldehyde (10 g L^{-1})
- (iv) thiourea (0.1 mL L^{-1}).

Operating conditions:

- (i) pH 13
- (ii) temperature ($28 \pm 2^\circ\text{C}$).

The influence of copper ion concentration, reducing agent, pH and temperature on the rate of deposition was studied. In this study, paraformaldehyde was used as a reducing agent. Paraformaldehyde is a polymeric solid form of formaldehyde having the same uses as formaldehyde. X-ray diffraction (XRD, PANalytical, Natick, MA, USA) was employed to determine the precipitated phase of the deposit and also residual stresses present within the coating material.

The surface morphology of the deposit was evaluated under high magnification to assess the grain size, deposit nature, heterogeneities and pores present in the deposits by scanning electron microscopy (SEM) using an S-3000 model with an acceleration voltage range of 20 000 V and with the magnification range of $\times 1000$. The plated specimens were cut into 1×1 cm size, mounted suitably and examined under the microscope. The deposit was also characterised by atomic force microscopy (AFM) using the model Picoscan 2000 (M/S Molecular Imaging, Tempe, AZ, USA). The AFM images of electroless copper deposit were measured by contact angle mode using silicon nitride tip of 30 nm diameter.

Results and discussion

Effect of copper methane sulphonate concentration on rate of deposition

It is found from Table 1 that with increasing concentration of copper methane sulphonate, the rate of deposition increases up to a copper concentration of 5 g L^{-1} . But $>4 \text{ g L}^{-1}$ the stability of the bath is decreased and at 5 g L^{-1} of copper the bath is unstable. Hence the bath containing 3 g L^{-1} of copper was used as optimum concentration for further studies. At this concentration the bath produces a good, adherent and bright deposit.

Effect of pH on rate of deposition

From Table 2, it is clear that with increasing pH of the bath, the rate of deposition also increases up to a pH of

Table 2 Effect of pH on rate of deposition and bath stability

pH	Rate of deposition/ $\mu\text{m h}^{-1}$	Stability of bath
12	0.4	Stable
12.5	2.1	Stable
13.0	3.3	Stable
13.5	2.6	Less stable

Table 3 Effect of concentration of paraformaldehyde on rate of deposition and bath stability

Concentration of paraformaldehyde/g L ⁻¹	Rate of deposition/ $\mu\text{m h}^{-1}$	Stability of bath
5	2.5	Stable
10	3.3	Stable
15	4.0	Moderately stable
20	4.4	Unstable

13. Above this pH, the stability of the bath is reduced and hence a reduction in the rate of deposition is observed. The used bath decomposed on storing overnight. Hence the pH selected for further study was 12.5–13.

Effect of concentration of reducing agent on rate of deposition

With the increasing concentration of paraformaldehyde, the rate of deposition increased slowly as shown in Table 3. The bath showed good stability up to 10 g L⁻¹. The bath containing 15 g L⁻¹ had moderate stability, i.e. upon keeping the bath for overnight and on filtration, a little copper powder was found in the container. The bath containing 20 g L⁻¹ of paraformaldehyde was of very poor stability after using for deposition, decomposition being higher than that at 15 g L⁻¹. Hence further studies were carried out with 10 g L⁻¹ of paraformaldehyde.

Effect of temperature on rate of deposition

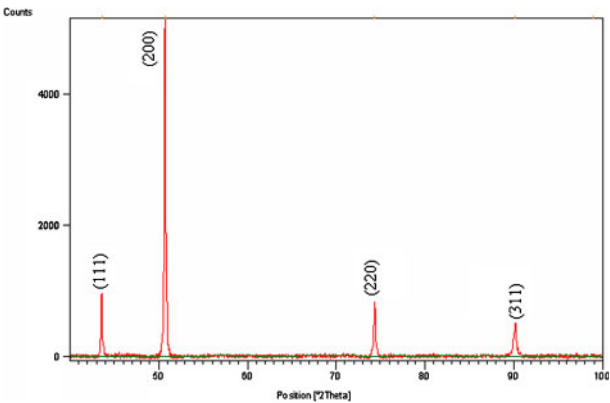
These experiments were carried out with the optimised concentration of copper and pH values and with 10 g L⁻¹ of paraformaldehyde. The results are tabulated at various temperatures in Table 4. The rate of deposition increases as the temperature increases. The bath is stable up to 50°C. Above 50°C, high rate of deposition was observed, but the used bath decomposed slowly on long standing. At 70°C the bath decomposed after 10 min of the start of the experiment. At room temperature good rate of deposition is achieved and it is higher than the conventional baths. Further experiments were carried out at room temperature.

Comparison of copper sulphate and copper methane sulphonate bath

The rates of deposition, solubility and stability of the bath were compared with the conventional sulphate bath keeping the composition of the bath and operating conditions constant. It can be observed from Table 5 that the deposition rate, stability and solubility are much higher for the methane sulphonate bath than the sulphate bath. When a continuous electroless deposition

Table 4 Effect of temperature on rate of deposition and bath stability

Temperature/°C	Rate of deposition/ $\mu\text{m h}^{-1}$	Stability of bath
28	3.3	Stable
40	4.0	Stable
50	7.2	Stable
60	13.7	Very slow decomposition
70	...	Decomposes



1 X-ray diffraction pattern of electrolessly deposited copper in basic bath

process is carried out, to maintain the rate of deposit and surface morphology the bath needs to be replenished with metal ion and reducing agent, and the pH of the bath needs to be maintained. Since the copper methane sulphonate salt solubility is high, it can be replenished after long intervals and with less volume. Since the experiment was carried out at room temperature, extra volume added for replenishment led to excess of bath, which needed to be removed. The removal of bath is called bail out, which is greatly reduced in the case of the methane sulphonate bath used here.

X-ray diffraction studies

The XRD pattern of the copper film deposited from the copper methane sulphonate metal ion is shown in Fig. 1. The XRD patterns are very similar to those of JCPDS data for standard copper metal. The effective crystallite size of the copper deposits has been estimated from the broadening of the diffraction peak from the (200) planes by the use of Scherer's equation^{27–29}

$$D_{hkl} = K\lambda / \beta \cos \theta$$
 (2)

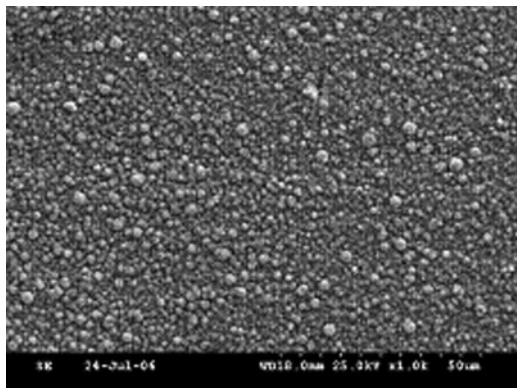
where λ is the X-ray wavelength for measurement (Å), i.e. for Cu K₂ radiation (1.5418 Å), β is the breadth of diffracted rays owing to the crystallite size (rad), i.e. FWHM (rad), θ is the Bragg angle of diffracted rays and K is the constant (0.89).

From the XRD pattern, it is observed that the preferred orientation is (200) plane. This may be considered owing to the copper methane sulphonate metal ion having a stronger influence on crystal orientation than other baths. As per Lee,³⁰ it could be concluded that copper methane sulphonate bath furnishes a greater number of copper ions, because of high conductivity and solubility leading to (200) plane. The

Table 5 Comparison of copper sulphate and copper methane sulphonate bath*

Parameters	Copper sulphonate bath	Copper sulphate bath
Rate of deposition/ $\mu\text{m h}^{-1}$	3.3	1.5
Stability of bath	Highly stable	Stable
Solubility/g dm ⁻³	507.1	336.9
Replenishment volume	Less volume	Large volume

*Copper content 3 g L⁻¹, disodium salt EDTA 20 g L⁻¹, paraformaldehyde 10 g L⁻¹, thiourea 0.1 mL L⁻¹, pH 13 and temperature 28±2°C.



2 Photograph (SEM) of electroless copper deposits, $\times 1000$

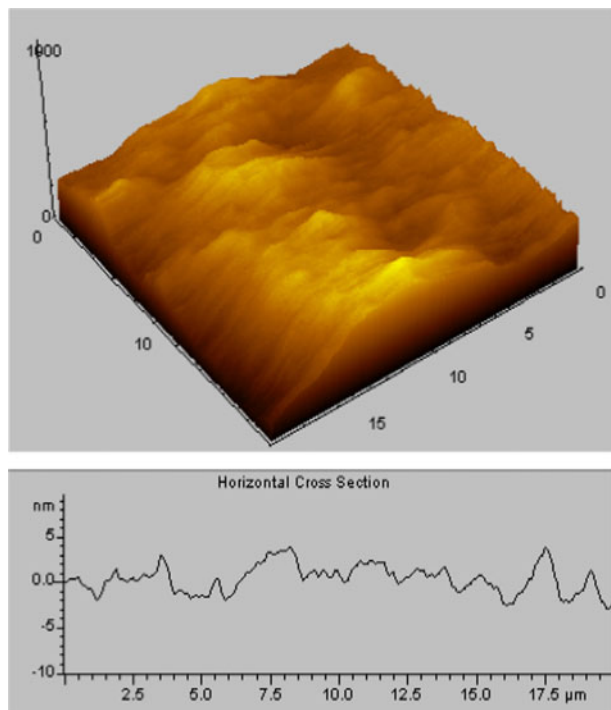
copper oxide phases are not observed in the deposit pattern. Thus the film is purely of copper metal. This was also confirmed by EDAX analysis. The intensity for the preferred orientation (200) plane for copper deposits in the plain bath is 5154 counts and the crystallite size is 134 nm.

SEM and AFM studies

An SEM photograph at a magnification of $\times 1000$ for the electrolessly deposited copper is shown in Fig. 2. The deposit surface is very smooth and some nodular growth of copper crystals is observed. Figure 3 shows the deposit characteristics obtained from the AFM studies. From this figure, it is evident that the deposit is highly smooth and the surface roughness is found to be on average only 10 nm.

Mechanism of electroless copper deposition

In this study, copper methane sulphonate $\text{Cu}(\text{CH}_3\text{SO}_3)_2$ was used as the source of copper ions and EDTA as complexing agent. Thus the deposition takes place via a



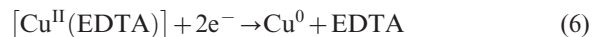
3 Image (AFM) of electroless copper obtained from methane sulphonate bath

copper EDTA complex and the mechanism of deposition is as follows.

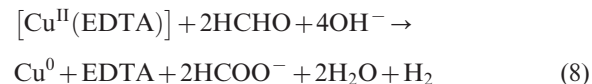
Anodic reactions



Cathodic reactions



The overall reaction taking place during electroless copper deposition is given below



After the reaction is initiated by the palladium catalyst the reaction becomes autocatalytic, which is believed to be due to the presence of hydrogen gas in the solution. Reaction (5) is a Cannizzaro reaction producing methanol and formate. Most of the commercial formaldehyde is stabilised with methyl alcohol. Methanol can be added to the bath to avoid this reaction, quantitatively varying from 40 to 250 mL L⁻¹.³¹

Conclusions

A novel copper electroless bath has been developed based on copper methane sulphonate as a source of metal ion with conventional reducing agent, i.e. formaldehyde. Methane sulphonic acid shows promise as a bath for achieving quality deposits of copper, with good rate of deposition, appearance and grain size and bath stability.

The results can be concluded as follows:

1. For the optimised chemical composition and operating conditions, the rate of electroless copper deposition was 3.3 $\mu\text{m h}^{-1}$.
2. The copper methane sulphonate bath has a stronger influence on crystal orientation than other baths. Hence, the XRD pattern showed a single peak centred at 50° , 2θ with a preferred orientation of (200). The deposit is purely of copper metal which is also evident from the EDAX analysis.
3. The SEM photograph of the deposit surface reveals a very smooth surface, and nodular growth of copper crystals is observed. The smoothness of the deposit was confirmed by AFM studies and it could be observed that the surface roughness was on average only 10 nm.

References

1. L. Darmstaedter: 'Handbuch zur Geschichte der Naturwissenschaften und der Technik'; 1908, Berlin, Verlag Springer.
2. L. Vanino and E. der Seitter: 'Formaldehyde A'; 1922, Wien Leipzig, Hartlebens Verlag.
3. G. Woldt: *Jahrbuch der Oberflächentechnik*, 1968, 178; 1970, 255; 1971, 172; 1972, 191.
4. W. Goldie: 'Metallic coating of plastics'; 1968–1969, Middlesex, Electrochemical Publications Ltd.

5. F. A. Lowenheim: 'Metal coating of plastics'; 1970, Park Ridge, NJ, Noyes Data Corp.
6. E. B. Saubestre: *Met. Finish.*, 1962, **60**, (4), 17.
7. P. B. Upton: *J. Electrodepos. Tech. Soc.*, 1947, **32**, 45.
8. F. D. Chattaway: *Proc. R. Soc. A*, February 1908, **80A**, 88–92.
9. R. M. Lukes: *Plating*, 1964, **51**, (11), 1066–1068.
10. E. B. Saubestre: *Proc. Am. Electroplat. Soc.*, 1959, **46**, 264–276.
11. F. I. Nobel, B. D. Ostrow and D. N. Schram: 'Bath and process for plating lead and lead/tin alloys', US patent no. 4,565,610, 1986.
12. A. P. E. Hanson and F. Jachimowicz: 'Retention and drainage aid', US patent no. 4,565,604, 1986.
13. F. I. Nobel, B. D. Ostrow and D. N. Schram: 'Process and electrolyte for electroplating tin, lead or tin-lead alloys', US patent no. 4,617,097, 1986.
14. C. T. J. Low and F. C. Walsh: *Trans. Inst. Met. Finish.*, 2008, **86**, (6), 315–325.
15. C. Doyle, N. Brown and M. Bardizeh: *Met. Finish.*, 2002, **100**, (1), 10–12.
16. J. Horkans, I. Hsu, P. C. Andricacos and H. Deligianni: *J. Electrochem. Soc.*, 1995, **142**, (7), 2244–2249.
17. C. T. J. Low, C. Kerr, B. D. Barker, J. R. Smith, S. A. Campbell and F. C. Walsh: *Trans. Inst. Met. Finish.*, 2008, **86**, (3), 148–152.
18. C. Rosnstein: *Met. Finish.*, 1990, **88**, (1), 17–21.
19. T. Kondo, S. Masaki, H. Inoue and K. Yamakawa: *Met. Finish.*, 1991, **89**, (10), 32–36.
20. N. Mart: WO 99/02765, assigned to AtotechGmbH, 1999.
21. W. A. Proell, C. L. Faust, B. Agruss and E. L. Combs: *Monthly Rev. Am. Electroplat. Soc.*, 1947, **34**, 541.
22. M. Hasan and J. F. Rohan: *J. Electrochem. Soc.*, 2010, **157**, (5), D278–D282.
23. N. M. Martyak, M. D. Gernon and P. Janney: 'Electroplating of copper from alkanesulfonate electrolytes', US patent no. 6,605,204, 2003.
24. M. D. Gernon, M. Wu, T. Busta and P. Janney: *Green Chem.*, 1999, **1**, (6), 127–140.
25. R. Balaji and M. Puspavanam: *Trans. Inst. Met. Finish.*, 2003, **81**, (5), 154–158.
26. K. N. Srinivasan and S. John: *J. Alloy. Compd*, 2009, **486**, 447–450.
27. M. Matsuoka, J. Murai and C. Iwakura: *J. Electrochem. Soc.*, 1992, **139**, (9), 2466–2470.
28. B. D. Cullity: 'Elements of X-ray diffraction'; 1978, London, Addison–Wesley.
29. A. Hung: *Plat. Surf. Finish.*, 1988, **75**, 62–65.
30. D. N. Lee: *J. Korean Inst. Eng.*, 1996, **29**, 301.
31. H. Marshall: *Electroplat. Met. Finish.*, 1975, **28**, (9), 7.