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ECO-FRIENDLY NOVEL BATH FOR ELECTROLESS COPPER DEPOSITION USING FORMALDEHYDE AS REDUCING AGENT

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Abstract:

In this study a novel eco friendly copper electroless bath has been studied using copper methane sulfonate is used as source material which has high solubility, EDTA as chelating agent,para formaldehyde as reducing agent, additives such as thiourea, cetrimide, 2MBT and NaOH is used as a pH adjuster. Bath is maintained in a pH range of 13-13.5. The bath is optimized for the parameters affecting the rate of deposition. In this present paper the rate of deposition, deposit quality, grain size, adherence is studied by which an ecofriendly bath is improved.

Key Words: Chelating Agent, Reducing Agent & Electroless Bath

1. Introduction:

Electroless plating is a variety of chemical deposition technology, involving the deposition of metals from solutions on to metallic/ non metallic surfaces without applying an external electric voltage [1, 2] not constrained by the sizes, shape or conductivity of the substrate. Potential applications of plating have recently emerged in IC fabrication and EMI shielding because it doesn't require vacuums or high temperature for thin metal film deposition. Electroless Copper plating is widely used to fabricate PCB, also favoured for copper coatings on various non- conductive substrates, such as plastics, glass and ceramics [3, 8].

Methane sulfonic acid is gaining more importance in the field of electroplating and electroless plating. Proell & co workers plated various metals from methane sulfonic acid baths (MSA) [9-15]. Electroless Nickel deposition [16] is also carried with methane sulfonic acid. But these baths are commercialized only from early1980's. Methane sulfonate bath [17] is characterized by (i) High metal salt solubility (ii) Excellent conductivity (iii) Stability (iv) less toxicity (v) Ease of effluent treatment. The deposit from MSA posses high adherence, smoothness, less nodular and less porous. Formaldehyde a well established reducing agent has significant environmental impact and its permissible level in air has been lowered to 0.5ppm in certain countries. Continuous exposure to formaldehyde causes irritation to eyes, throat and lungs [18].

2. Experiment:

A new bath for electroless copper deposition over PCB was made using copper methane sulfonate as a source of metal ion which has excellent solubility than copper sulfate. The bath consists of copper methane sulfonate, EDTA, formaldehyde and NaOH to raise the pH. The bath was optimized for metal ion concentration, pH of the bath and concentration of reducing agent by weight gain method. The effect of temperature on rate of deposition and stability of the bath is studied by adding Thio urea of 0.1 ppm as stabilizer.

The gravimetric experiments of electroless copper plating is carried out in 100 mL plating bath with 12.5 cm^2 copper sheet. The thickness of copper deposit layer and the rate of electroless copper deposition were estimated by weight gain method. The rate of deposition was calculated using the following formula

Rate of deposition (μhr^{-1}) = W x 60 x 10^4 / DAt (1)

Where, W is the weight of the deposit (g), D is the density of the deposit (gcm^{-3}) T is the plating duration (hr) and A is the Surface area of the specimen (cm^2).

Copper specimens of 99.99% purity of area 12.5 cm^2 were degreased, oxide removed and activated in a solution of $0.1gL^{-1}$ $PdCl_2$ + 50 mL of HCl. The panel is washed and rinsed with double distilled water and then weighed and immersed in 100 mL of electroless copper plating bath for 30 minutes. The solutions were prepared using analytical grade reagent and double distilled water. The experiments were carried out at room temperature $28^0C(+0.5^\circ)$.The rate of deposition, and morphology of the degreased panel by using additives like thiourea, cetrimide and 2MBT is studied The surface morphology was observed with 1 cm^2 size of plated panel using scanning electron microscope (SEM).

3. Results and Discussion:

The rate of deposition and morphology is studied using thiourea, cetrimide and 2MBT as additives.

Effect of Thiourea on Rate of Deposition:

Table 1: Effect of Thio urea on Rate of Deposition at room temperature 28±2°C

S.No	Conc (ppm)	Plating rate(µm/hr)	stability	Deposit colour
1.	0.1	3.75	Stable	Dark deposit
2.	0.5	2.85	Stable	Dark deposit
3.	1.0	2.79	Stable	Dark deposit

Thiourea has three possible co-ordination sites in which 'S' is in the dominant co-ordination centre in its reaction as inhibitors. In this present investigation the deposition rate of at different concentrations of thiourea (0.1, 0.5, 1.0ppm) was studied. It was known that, as the concentration of thiourea increases the deposition rate was decreased as given in table.1.The decrease in the deposition rate may be related to the excess coverage on the copper surface, which makes the reduction of ions difficult or even impossible. This is a well known adsorption phenomenon of overcrowding as suggested by Nazzi [19] and Hung [20]. Thiourea acts as a very good stabilizer which prevents the decomposition of the bath but improves the stability of the bath. From the SEM studies it is observed that deposits from methane sulphonate bath containing thiourea as additive are fine grained from literature. Fig. 1 shows the microstructure of plain bath deposit. It is fine-grained and the grain size ranging from 50µm to 100µm.

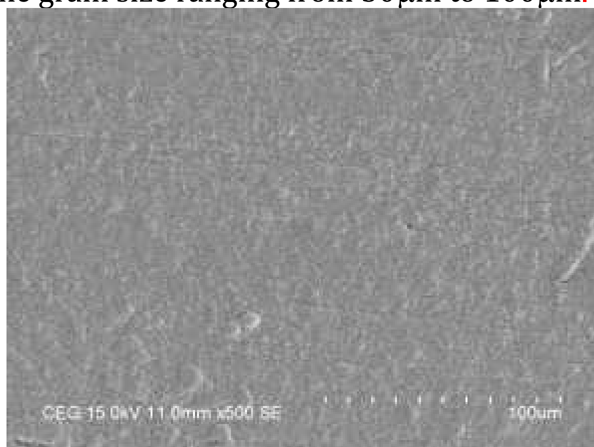

Figure 1: SEM photograph of electrolessly deposited copper using thio urea as additive

Effect of Cetrimide on Rate of Deposition:

Cetrimide is Cetyl trimethyl ammonium chloride .The change in the deposition rate of electroless copper plating is seen and the deposition rate decreased from 8.49 to 7.87 μm/hr.Because of its bulky structure its adsorption is lesser on the metallic surface. From the SEM studies it is observed that deposits from methane sulphonate bath containing cetrimide as additive are fine grained from literature. Fig. 2 shows the microstructure of plain bath deposit. It is fine-grained and the grain size ranging from 50μm to 100μm.

Table 2: Effect of Cetrimide on Rate of Deposition at room temperature 28±2°C

S.No	Conc(ppm)	Plating rate(μm/hr)	stability	Deposit colour
1.	0.1	8.49	Stable	Dark deposit
2.	0.5	8.03	Stable	Dark deposit
3.	1.0	7.87	Stable	Dark deposit

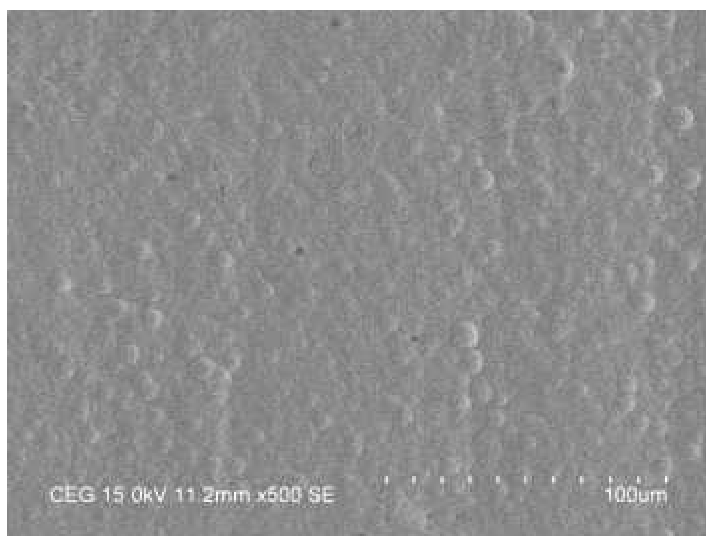

Figure 2: SEM photograph of electrolessly deposited copper using cetrimide as additive

Effect of 2MBT on Rate of Deposition:

2MBT is a heterocompound containing nitrogen and sulphur atoms in it. The change in the deposition rate of the electroless copper plating as a function of 2MBT is seen. The deposition rate decreased from 8.89 to 5.43 μm/hr as the concentration of 2MBT in the plating bath was increased as given in table.3.2MBT gets adsorbed at the catalytic site of substrate surface and thus hindering the oxidation of HCHO, by decreasing the plating rate which in turn stabilizes the bath. Because of its bulky structure its adsorption is lesser on the metallic surface. The presence of 2MBT increases bath stability, giving semi bright deposits. From the SEM studies it is observed that deposits from methane sulphonate bath containing thiourea as additive are fine grained from literature. Fig. 3 shows the microstructure of plain bath deposit. It is fine-grained and the grain size ranging from 50μm to 100μm.

Table 3: Effect of 2MBT on Rate of Deposition at room temperature 28±2°C

S.No	Conc(ppm)	Plating rate(μm/hr)	stability	Deposit colour
1.	0.1	8.89	Stable	Dark deposit
2.	0.5	7.55	Stable	Dark deposit
3.	1.0	5.43	Stable	Dark deposit

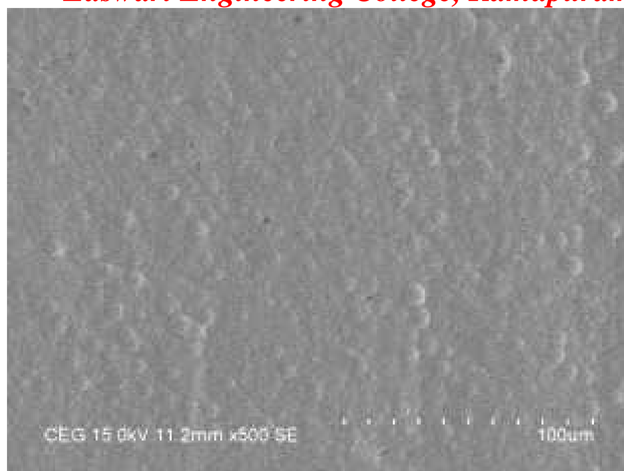

Figure 3: SEM photograph of electrolessly deposited copper using 2MBT as additive

4. Conclusion:

Conductive pure copper can be deposited by electroless technique from EDTA bath after controlling the operative conditions and by adding suitable additives. The additives like 2MBT, thiourea and cetrimide increases the stability with high plating rate and also the morphology is good with fine grain size. The additives improve the colour and the quality of the deposits.

5. References:

1. G. O. Mallory, J. B. Hajdu (eds), electroless plating: Eunda-metals and applications, American electroplaters and surface finishers society, Orlando, FL,1990.
2. J. B. Hajdu, plating surf. finish. 83(1996) 23.
3. E. Groshart, Met.Finish.70 (1972) 85.
4. G. V. Elmore, R.F. Hershberger, J. Electrochem, Soc.121 (1974) 107.
5. T. Osaka, Y. Tamiya, K. Naito, K.Sakaguchi, J.surf.finish.
6. S. Sugihara, A. Iwasawa, K.onose, J. Yamaki, J. Appl. Electrochem. 26 (1996) 63.
7. H. Yoshiki, V. Alxenandruck, K. Hashimoto, A. Fujishima, J. Electro chem. Soc. 141 (1994) L56
8. H. Yoshiki, K. Hashimoto. Fujishima, J. Electrochem.SOC. 145 (1998) 1430.
9. W.A. Proell, C.E. Adamsand B.H. Shoemaker. Ind. Eng. Chem. (1948) 40 1129. [10] C.S. Chen, C.C Wa & Y.Y. Wang, Plat. And surf. Finish. (2001) 88 86.
10. Tetsuya Kondo, Seishi masaki, Hiroyuki Inoue, Koji Yamabawa. Metal finish, 1991 89 32.
11. C. S. Chen, C C. Wan & Y Y. Wang, Trans IMF (1998), 76-54.
12. Charles Rosenstein, Metal Finish, 1990 88 17
13. M. I. Smirnow, K.M. Tyutina, A.N. Popov, Russ, J. of electro chem. (1995) 31 543.
14. Jeong-Han Kim, MIN-suk suh, Hyuk-San know. Surf. And Coat. Tech. (1996) 78 53.
15. K. N.S rinivasan, S. John, Journal of alloys and Compounds, 486(2009)447-450
16. Mi chael D. Gernon etal, Green Chemistry June (1999) 127.
17. Darken. J. Trans, Inst. Metal Finish, 69(2), (1991) 66.
18. F. J. Nuzzi, Plating and Surface Finishing 70 (1983)5
19. A. Hung, J. Electro chem. Soc.132 (1985) 1047.