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Formaldehyde Free Eco-Friendly Novel Bath For Electroless Copper Deposition

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Abstract— **In this study a novel eco friendly electroless copper bath has been studied using copper methane sulfonate as source material which has high solubility, EDTA as chelating agent, non formaldehyde reducing agent such as glyoxylic acid and NaOH is used as a pH adjuster. Bath is maintained at a pH range of 13 - 13.5. The bath is optimized for the parameters affecting the rate of deposition. The bath is compared with formaldehyde bath. The quality of the deposit improved with much more refined grain size greater than that of formaldehyde bath and a promising eco-friendly bath is developed.**

Key words-Electroless copper; Methane sulfonic acid; Glyoxylic acid;,Formaldehyde; EDTA

I. 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 early 1980'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]. Glyoxylic acid [19-21] which is similar in properties to formaldehyde and free from health hazard is used here. The results were compared with formaldehyde as reducing agent.

II. EXPERIMENTAL

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, glyoxylic acid 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

$$\text{Rate of deposition } (\mu hr^{-1}) = W \times 60 \times 10^4 / DAt \quad (1)$$

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° C (+0.5˚C).

Effect of concentration of metal ions on rate of deposition was studied. Copper ions, viz., 1 to 5 gL^{-1} and correspondingly disodium salt EDTA concentration was increased viz, 7 gL^{-1}, 14 gL^{-1}, 20 gL^{-1}, 28 gL^{-1}, 35 gL^{-1} to have proper complexing of copper ions, at a constant pH of 13.5. Effect of pH on rate of deposition was studied for three different pH viz., 12.5, 13.0 and 13.5 for optimized metal ions. Effect of glyoxylic acid was studied for different concentration viz., 11 gL^{-1}, 12gL^{-1}, 13 gL^{-1}, 14 gL^{-1} and 15 gL^{-1} for optimized pH and metal ion. 0.1 ppm of thiourea was also added as stabilizer. Effect of temperature on rate of deposition was carried out for different temperature viz., 30° C, 40° C, 50° C, 60° C and 70° C for the optimized bath with out any stabilizer.

A comparative study is made with the same bath with para-formaldehyde (10 gL^{-1}) as reducing agent at 12.5-13 pH. The deposition was carried out at various temperatures viz., 30° C, 40° C, 50° C, 60° C, 70° C in order to find stability of bath and rate of deposition with out any stabilizer.

The crystal structure of the copper deposits were investigated using X-ray diffractometer X'pert pro XRD,(make- Panalytical, USA) Cu Kα radiation and graphite filter at 40 KV and 30 mA. A continuous scan mode in the range $30 < 2\theta < 80^o$ with a scan rate of 1˚ 2 θ per min^{-1} was used. The surface morphology was observed with 1 cm^2 size of plated panel using scanning electron microscope (SEM). The SEM photographs were taken using S-3000 model with an acceleration voltage range of 20,000 V and with the magnification range of 1000.

III. RESULTS AND DISCUSSION

A. Effect of copper methane sulfonate concentration on rate of deposition

Table I shows that as the concentration of copper methane sulfonate is increased, the rate of deposition increases gradually. The bath is stable up to the copper concentration 4 gL^{-1} and above which the stability of the bath is decreased. The bath with concentration 4 gL^{-1} showed a few copper particles on keeping the used bath over night. The bath containing 3 gL^{-1} of copper gave good adherent and bright pink deposit with high stability. Hence further plating was carried out with this concentration.

TABLE I. EFFECT OF CONCENTRATION OF COPPER AS METHANE SULFONATE ON RATE OF DEPOSITION

Concentration of copper (gL^{-1})	Rate of deposition (μm/h)	Stability of bath
1	0.63	stable
2	1.77	stable
3	2.01	stable
4	2.24	stable
5	3.22	stable

B. Effect of pH on rate of deposition

From Table II it is clear that at a pH of 12.5 no reaction is observed. Thus it needs higher pH range for the deposition. Further increase in the pH up to 13 gave very low rate of deposition. Increase in deposition rate is observed between the pH range of 13.0 – 13.5. Above 13.5 pH bath decompose, on commencement of plating. Hence the pH selected for further study was 13-13.5 pH.

TABLE II. EFFECT OF PH ON RATE OF DEPOSITION

pH	Rate of deposition (μm/h)	Stability of Bath
12.5	No reaction	-
13.0	1.1	Stable
13.5	1.8	Stable
13.8	-	Decomposes

C. Effect of concentration of reducing agent on rate of deposition

Stability of the bath for glyoxylic acid is so poor that slow decomposition of bath was even observed with 12 mL (50% v/v) of glyoxylic acid. Hence to study the effect of increase in concentration with rate of deposition 0.1 ppm of Thiourea was used as stabilizer. Upon increasing the concentration of glyoxylic acid, the rate of deposition increases slowly (Table III). Bath showed good stability from 10-15mL (50% v/v) of glyoxylic acid. There is no much variation in the rate of deposition with increase in concentration of reducing agent. Hence the bath with 11mL per liter showed better deposit characteristic was used for further studies.

TABLE III. EFFECT OF CONCENTRATION OF GLYOXYLIC ACID ON RATE OF DEPOSOTION WITH 0.1 PPM OF THIOUREA.

Glyoxylic acid (mL/L)	**Rate of deposition (μmh^{-1})**	**Stability of bath**
11	1.77	Stable
12	1.83	Stable
13	1.92	Stable
14	2.05	Stable
15	2.09	Stable

D. Effect of temperature on rate of deposition:

The experiments were carried out with the optimized concentration of copper ($3mgL^{-1}$) and pH values (13.0 – 13.5) and with 11 mL/L of glyoxylic acid. The results are tabulated at various temperatures in the Table IV. The rate of deposition increases as the temperature increases. The bath is stable only up to 40° C. The bath is stable even at 50˚ C but bath on standing after deposition undergoes slow decomposition. At 60° C high rate of deposition was observed, but the bath decomposes after 15 min from the start of deposition process.

TABLE IV. EFFECT OF TEMPERATURE ON RATE OF DEPOSITION OF COPPER IONS WITH GLYOXYLIC ACID

Temperature (° C)	**Glyoxylic acid(11mL/L**		**Formaldehyde**	
	Rate of Deposition (μmh^{-1})	***Stability of bath***	***Rate of deposition (μmh^{-1})***	***Stability of bath***
28	2.01	Stable	3.3	Stable
40	3.5	Stable	4.2	Stable
50	4.78	Slow decomposition copper particles are found	7.2	Stable
60	6.05	Decomposes after 15 min of plating Started	13.7	Slow decomposition copperparticles are found
70	-	Decomposes	-	Decomposes

IV. COMPARISON

From the table IV it is clear that the formaldehyde bath deposition occurs at 12.5 - 13 pH but for glyoxylic acid bath deposition occurs only at 13-13-5 pH. Hence glyoxylic acid bath requires slightly higher pH than formaldehyde. The stability of the bath for glyoxylic acid is less than the formaldehyde bath. Formaldehyde bath is stable up to 50° C but glyoxylic acid bath is stable only up to 40° C. The rate of deposition for formaldehyde bath is very high when compared to glyoxylic acid.

XRD patterns were taken for copper deposition with glyoxylic acid (Figure 1) and formaldehyde (Figure 2) as reducing agent. In both the patterns sharp peak is observed confirming deposited copper is crystalline in nature with a preferred orientation of 211 planes. The surface morphology of electroless copper deposition with glyoxylic acid and formaldehyde as reducing agent using SEM is given in Figure 3a & 3b. Both the photographs show nodular structure, but the grain size is much more refined in glyoxylic acid than formaldehyde.

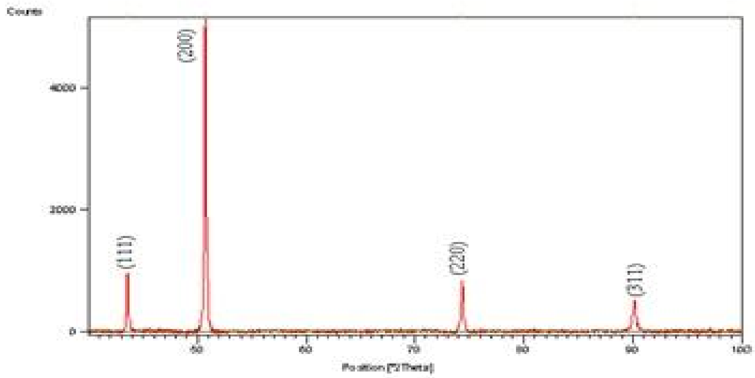

Figure 1. XRD pattern of electrolessly deposited copper with glyoxylic acid as reducing agent

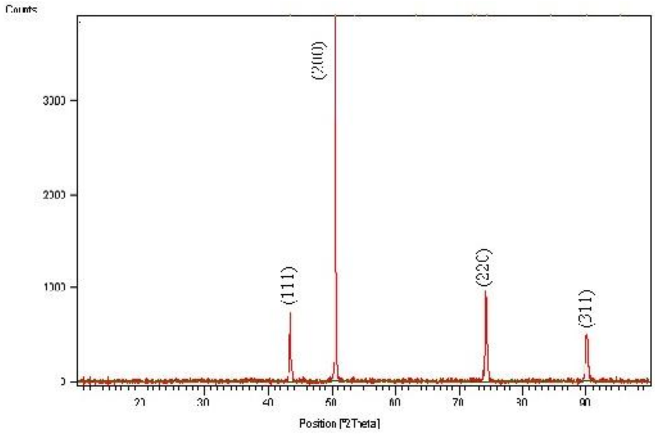

Figure 2. XRD pattern of electrolessly deposited copper with formaldehyde bath as reducing agent

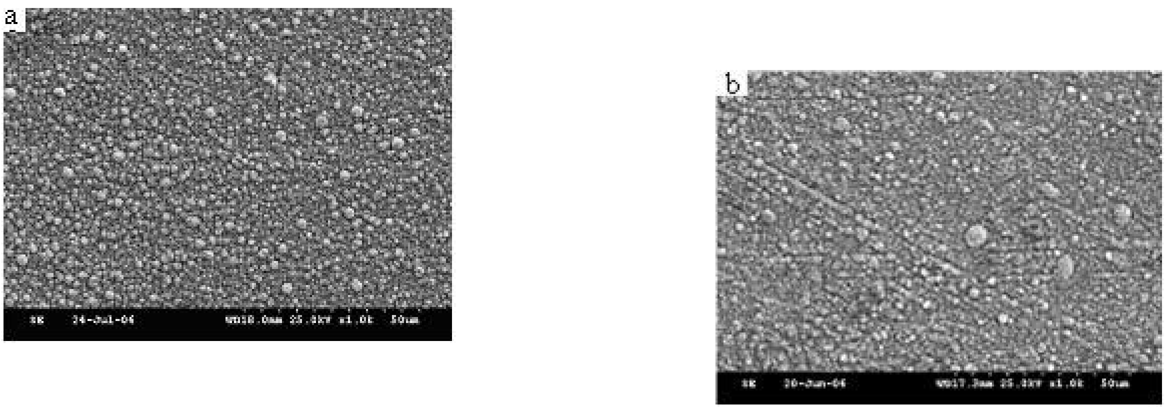

Figure 3. SEM photograph of electrolessly deposited copper with a) glyoxylic acid as reducing agent b) formaldehyde as reducing agent.

V. CONCLUSIONS

A new formaldehyde free electroless bath has been formulated with a new source of metal ion (based on copper methane sulfonate). Only a little amount copper methane sulfonate is required for replenishments due to higher solubility of copper methane sulfonate. The small replenishment volume maintains a constant operating temperature, and avoids bail out problem (in case of room temperature), which in turn produces uniform and high quality deposits and reduces waste. The bath is compared to that of conventional reducing agent formaldehyde bath, even though rate of deposition is low compared to formaldehyde bath high quality coatings with a refined grain size is observed. The bath is stable at room temperature and its stability is less only at higher temperature. In the current era much importance is given to the eco friendly technology, this plating bath will be the apt bath for electroless copper plating. Following is the optimum concentration of bath and operating conditions to get quality copper deposits:

Copper as methanesulfonate: 3 gL^{-1}, Di sodium salt of EDTA: 20 gL^{-1}, Glyoxylic acid: 11mL/L (50 %v/v), pH (Ammonia) : 13, Temperature : 28 $\pm$ 0.5° C.

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