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Controlling factors affecting the stability and rate of electroless copper plating

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The main purpose of this article is to focus on the electroless copper deposition from EDTA bath which is used in printed circuit boards (PCB) and very large scale integrated circuits (VLSI). The effect of the bath operating conditions and bath additives on plating rate, bath stability and morphology of the coating has been studied. It has been found that the organic additive does not stabilize the bath but enhances the plating rate. The additives were found to modify the structure of the deposits with the production of small grain size, dense and tightly adherent copper deposit.

Keywords: Printed circuit boards, bath additives, stability, morphology, grain size.

Introduction

In the middle of the twentieth century a revolutionary method of coating technique was developed by Brenner and Riddell[1]. This coating technique is popularly known as "Electroless coating". Electroless plating is an autocatalytic method in which the reduction of metallic ions in the solution and the film deposition can be carried out through the oxidation of chemical compound present in the solution itself i.e. reducing agent which supplies an internal current. The autocatalytic or chemical reduction of aqueous metal ions coated to a base substrate without passage of external current is referred to as electroless plating[2,3]. Electroless coating process has gained wide acceptance in the market due to the coatings' excellent corrosion and wear resistance properties and it is also good for soldering and brazing purposes[4]. The difference of electroless plating process[5,6] from the immersion plating[7] is that the deposition of metal is autocatalytic reduction process and electroless plating does not use electrodes, and is an autocatalytic reaction on the metal surface after nucleation has begun. An immersion plating solution, on the other hand, operates on the principle of displacement of the surface skin of the substrate by a more noble metal that is in solution.

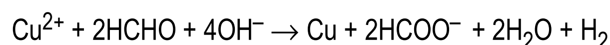
Electroless plating has several advantages over electroplating technique, except the type of the bath. The advantages include better coating rate, improved quality of the deposit, namely physical and chemical properties, uniform coating rate[8] etc. The electroless plating bath contains a source metal ion, reducing agent, complexing agent, accelerators, stabilizers, buffering agent and its parameters include controlled temperature and pH. Their role is briefly summarized in Table 1.

Table 1. Components and parameters of bath and their functions

Sl. no.	Components/ Parameters	Function
1.	Metal ions	Source of metal
2.	Reducing agent	Supplies electrons to reduce the metal ions
3.	Complexing agent	Prevent excess of free metal ion concentration, improves adhesion
4.	Accelerators	Accelerate the reducing agent and increase the deposition rate
5.	Stabilizers	Stabilizes the bath from decomposition by shielding catalytically active site

Mechanism of electroless copper deposition:

Lukes[9] found the following overall reaction for electroless copper solution and HCHO as the reductant



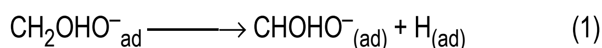
$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu + 2HCOO^- + 2H_2O + H_2$$

Rochelle salt (K-Na tartarate) was used as complexing agent in the earliest baths which shows low plating rates and low temperature applications[10]. For higher plating rates ap-

plied at higher temperatures, the most commonly used complexing agents are based on ethylenediamine tetra acetic acid[12]. In the same way various common reducing agents have been used in electroless baths namely formaldehyde, dimethyl amine boron, borohydride, hypophosphite and hydrazine[10–12]. But in practice all commercial electroless copper solution for deposition of high purity copper have utilized formaldehyde as the reducing agent. Copper methane sulfonate has been used as a source of metal ion which has excellent solubility, stability, conductivity and less toxicity than other copper salts.

Additives are of two types viz. stabilizers and accelerators. Additives which stabilize the bath against the formation of cuprous oxide particles are referred to as stabilizers. Among the materials reviewed as stabilizers are compounds such as thiourea[13], 2-mercapto benzothiazole[14], 2,2′-dipyridyl[15–18] which contains like sulphur and nitrogen element with lone pair of electrons. Accelerators are those substances which enhance the plating rate. Among the materials reviewed as accelerators are compounds such as oxalic acid, malonic acid, succinic acid, acetic acid and citric acid containing oxygen element with lone pair of electrons.

The reaction mechanism has not been clarified. It is believed as follows: formaldehyde tends to be more susceptible to oxidation as the pH is raised and accordingly, when a carboxylic acid is added to the plating bath it prevents the pH of the plating bath decreasing in the vicinity of the interface between copper and HCHO with the result that the HCHO becomes more susceptible to the catalytic action of copper, thus emitting electrons more easily. Thus accelerator accelerates the oxidation reaction of reducing agents and in turn enabling electron release with ease and reduction of copper ion takes place quickly, increasing the rate of deposition. It accelerates the oxidation reaction in the mechanism as shown in eq. (1),



$$CH_2OHO^-_{ad} \longrightarrow CHOHO^-_{(ad)} + H_{(ad)} \quad (1)$$

Experimental

The solutions were prepared with analytical grade reagents and deionised water. A bath for electroless copper deposition over PCB was made using copper methane sulfonate as a source of metal ion. The optimized[19] bath consists of 3 g/L of copper methane sulfonate, 20 g/L of disodium salt of EDTA, 10 g/L of formaldehyde and NaOH to alter the pH is used in this current study.

The gravimetric experiments of electroless copper plating is carried out in 100 ml plating bath with 2.5×2.5×0.1 cm^3 copper sheets. The thickness and the rate of electroless copper deposition were estimated by weight gain method. The rate of deposition was calculated using the following formula

$$\text{Rate of deposition } (\mu/\text{h}) = \frac{W \times 60 \times 10^4}{DAt}$$

where, W = weight of the deposit (g), D = density of the deposit (g/cm^3), t = plating duration (h) and A = surface area of the specimen (cm^2).

Pretreatment of the coating surface:

Copper specimens of 99.99% purity of area 2.5×2.5×0.1 cm^3 were polished with grit paper, degreased and activated in a solution of 0.1 g/L acidic $PdCl_2$ for 30 s. The panel is washed and rinsed with double distilled water and then weighed and immersed in 100 ml of electroless plating bath for one hour. The experiment was carried out at room temperature at 28°C (±0.5°C) .The Effect of accelerators on deposition rate was studied by gravimetric experiments.

Cyclic voltammetry:

The oxidation currents and potentials of formaldehyde oxidation and reduction current and potentials of Cu^{II} were investigated using cyclic voltammetry. The CV was recorded for a fixed potential range of –1 V to +1 V with a scan rate of 100 mV/s.

XRD:

The crystal structure of the copper deposits were investigated using X-ray diffractometer X'pert pro XRD, (make - P analytical, USA) Cu Kα radiation and graphite filter at 40 KV and 30 mA. A continuous scan mode in the range $30 < 2\theta < 80°$ with a scan rate of 1°/2θ per min^{-1} was used.

SEM:

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-3400N model with an acceleration voltage range of 20,000 V and with the magnification range of 10000.

Results and discussion

Additives which enhance the plating rate are called as accelerators. The deposition rate is generally very low for electroless copper depositions (1.6–2.5 μ/h)[20,21] in the pres-

ence of stabilizer. To improve the rate of deposition, dicarboxylic acids like oxalic acid and succinic acid is added to electroless copper plating bath.

In the present study the effects of dicarboxylic acids namely oxalic acid and succinic acid are studied. In Table 2 the deposition rate of accelerators at different concentration viz. 0.001 *M*, 0.01 *M* and 0.05 *M* are shown in the presence of small amount of stabilizer. In the accelerators it is observed that as the concentration increases, rate of deposition increases and the bath is quiet stable. It was observed that the rate of deposition is high for the bath containing accelerators when compared to the plain bath.

Table 2. Effect of accelerators on rate of deposition at room temperature 28±2°C

Sl. no.	Accelerators	Concentration 0.001	0.01	0.05	Stability
1.	Plain bath		3.3		Stable
2.	Oxalic acid	5.0	5.3	5.5	Stable
3.	Succinic acid	4.4	4.7	5.1	Stable

Bath is stable with small amount of stabilizer up to 0.05 *M* of acid. Oxalic acid being smaller in size[22] could easily adsorb on catalytic site and accelerate the oxidation of formaldehyde easily. Succinic acid is bigger in size compared to oxalic acid, the adsorption is weak at the catalytic site hence accelerates to a lesser extent than oxalic acid. The result obtained by this method is in good agreement with the results obtained by glyoxylic acid as reducing agent[19].

Cyclic voltammetry:

Potential sweep cyclic voltammetry is one of the most power electrochemical techniques for obtaining electrochemical spectrum of a charge transfer system and also for establishing detailed examination of reaction mechanism. CV technique is carried out to understand the chemistry of electroless copper plating solutions[23–25] and the role of the additives in electroless bath. Cyclic voltammetry are carried out with three electrode assembly. The working electrode is 1 cm^2 in area of copper electrode. The Pt foil is 1 cm^2 in area acts as counter and SCE as reference electrode. The potential range of –1 V to +1 V was kept constant for all experiments with a scan rate of 100 mV/s. CV studies were carried out for plain bath and accelerator bath at different concentration at room temperature. Table 3 shows the cyclic voltammogram of electroless copper bath in presence and absence of accelerators.

Table 3. Cyclic voltammogram of electroless copper bath with formaldehyde in presence and absence of accelerators (1 ppm)

Sl. no.	Accelerator	Peak current (HCHO oxidation) (mA/cm^2)	Peak potential (HCHO oxidation) (mV)
1.	Plain bath	8.5	–0.26
2.	Oxalic acid	13.5	–0.27
3.	Succinic acid	12.7	–0.26

The accelerating power is high for dicarboxylic acid due to the presence of two COO^- ions enabling oxidation of *p*-formaldehyde. The CV of plain bath is shown in Fig. 1. The CV of oxalic acid (Fig. 2) and succinic acid (Fig. 3) shows that oxalic acid acceleration is higher than succinic acid. Suc-

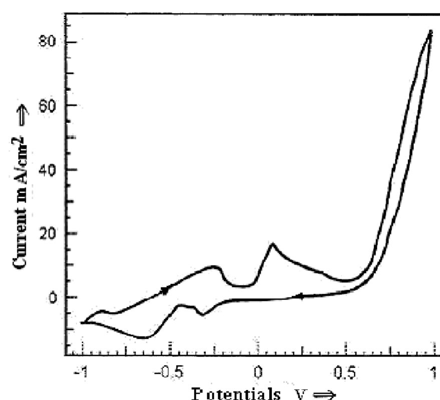


Fig. 1. Cyclic votammogram of electroless copper plain bath; scan rate 100 mV/s, pH 12.5 to 13.0, temperature (28±2°C).

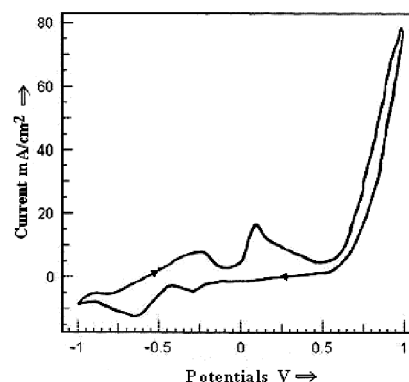


Fig. 2. Cyclic votammogram of electroless copper plain bath; scan rate 100 mV/s, pH 12.5 to 13.0, temperature (28±2°C) with oxalic acid 1 ppm.

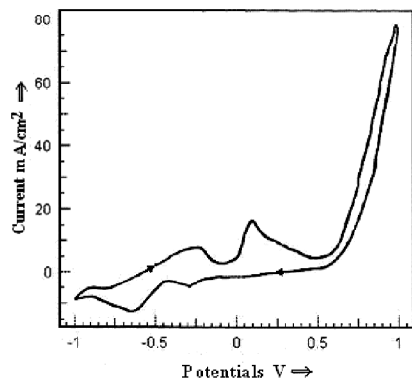


Fig. 3. Cyclic votammogram of electroless copper plain bath; scan rate 100 mV/s, pH 12.5 to 13.0 temperature (28±2°C) with succinic acid 1 ppm.

cinic acid being larger molecule adsorption at the active site is weaker compared to oxalic acid.

X-Ray diffraction pattern:

The XRD pattern for copper film from different bath has a preferred orientation of (111), (200), (220) plane[26–28]. It is observed that in presence of any additive the copper plane takes any one of the above said planes as preferred plane or leads to a random orientation of all the planes. XRD patterns were taken for copper deposition with formaldehyde as reducing agent and shown in Fig. 4. In this pattern sharp peak is observed confirming deposited copper is crystalline in nature with a preferred orientation of 200 planes. Fig. 5 and Fig. 6 shows the XRD pattern for oxalic acid and succinic acid which also confirms the orientation of 200 planes.

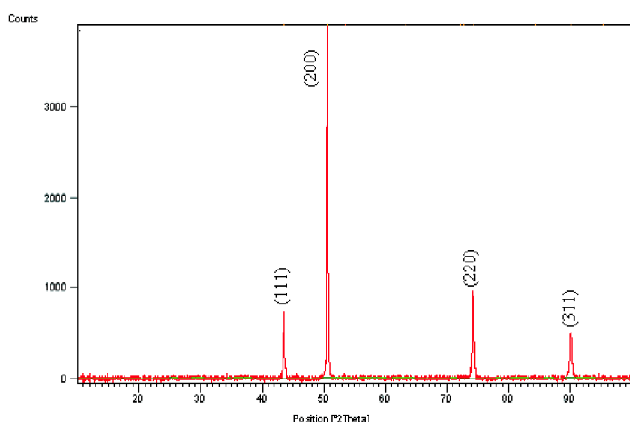


Fig. 4. XRD pattern of electrolessly deposited copper plain bath with formaldehyde bath as reducing agent.

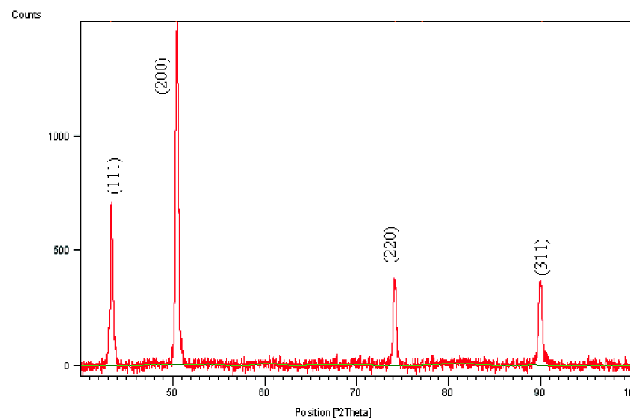


Fig. 5. XRD pattern of electrolessly deposited copper with succinic acid (0.05 *M*).

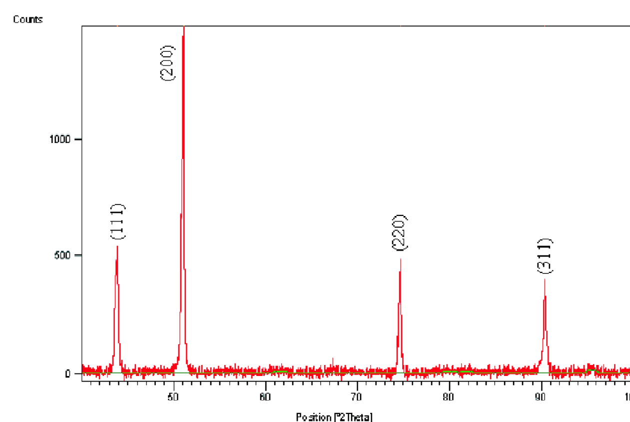
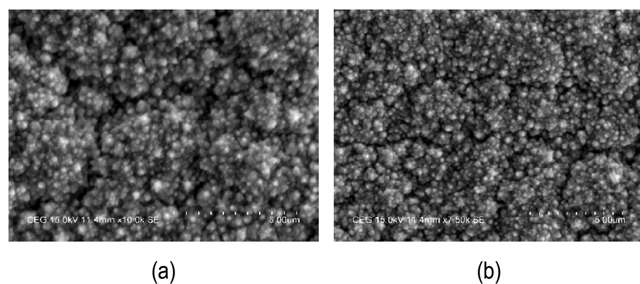


Fig. 6. XRD pattern of electrolessly deposited copper with oxalic acid (0.05 *M*).

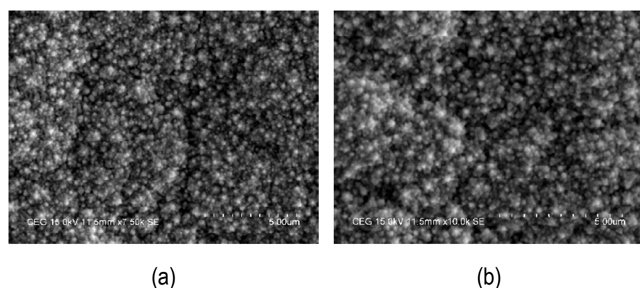
SEM photomicrographs:

SEM photographs at a magnification of X7500 and X10000 for the electrolessly deposited copper specimens with HCHO as reducing agent for accelerators are as shown in Figs. 7 and 8. The deposit surface is very smooth and the deposits show nodular growth as seen in the photograph. Both oxalic acid and succinic acid shows fine grained deposits. The crystals are more regular. It is observed that deposits from methane sulphonic acid bath are fine grained compared to commercial $CuSO_4$-EDTA bath[21]. Porosity is much less with this bath. The structure morphology, grain size is in good agreement with the rate of deposition obtained by weight gain method.



(a) (b)

Fig. 7. SEM photograph of electrolessly deposited copper using oxalic acid with (a) X7500 and (b) X10000.



(a) (b)

Fig. 8. SEM photograph of electrolessly deposited copper using succinic acid with (a) X7500 and (b) X10000.

Conclusion

Conductive pure copper can be deposited by electroless technique from copper methane sulphonate bath with EDTA as complexing agent after controlling the operative conditions with carboxylic acid as accelerators. Oxalic acid and succinic acid has been proved to be an excellent accelerator for electroless copper deposition with good bath stability. This has been proved by weight gain method and cyclic voltammetry. Surface morphology shows fine deposits.

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