Full Length Research Paper

Surface modification with copper by electroless deposition technique: An overview

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Surface behaviour is very important for which substrate surface preparation is emphasized in electroless deposition process. It directly or indirectly affects surface behaviour as well as the kinetics of electroless deposition process. So far as mechanism is concerned, it proceeds in an electrochemical pathway. The electrochemical approach provides clarity of the mechanism by studying independently the partial anodic and cathodic reactions in electroless deposition of copper. The reducing and complexing agents play a vital role for the kinetics and mechanism of the process. The traditional reducing agent, formaldehyde, can be substituted by glyoxylic acid since the latter (1.1 V) shows close electrode potential as that of formaldehyde (1.7 V) and is eco-friendly. In case of triethanolamine as a new complexing agent enhanced the deposition rate and gives a thicker bright deposit of copper.

Key words: Electroless, copper, glyoxylic acid, kinetics, mechanism.

INTRODUCTION

Archaeological evidence demonstrates that copper was used as far back as 1, years ago for items such as ornaments in western Asia. During the prehistoric Chalcolithic period, man discovered how to extract and use copper to produce ornaments and implements. As early as the 4th to 3rd millennium BC, workers extracted copper from Spain's Huelva region. Israel's Timna Valley provided copper to the Pharaohs. In South America, the pre-Columbian Maya, Aztec and Inca civilisation exploited copper. During the middle Ages, copper and bronze works flourished in China, India and Japan. The discoveries and inventions relating to electricity and magnetism of the late 18th and early 19th centuries by scientists such as Ampere, Faraday and Ohm and the products manufactured from copper, helped launch the Industrial revolution and propel copper into new era.

Today, copper continues to serve society's needs. It includes electrical, electronics and communications, transportation, industrial machinery and equipment's, consumer and general products, consumption by end use sectors. Besides all these, copper is essential to plants, animals and human health too. Deficiencies, as well as excesses, can be detrimental to health. The copper content of an adult ranges from 5 to 12 mg. The average dietary intake of copper by adults in some countries ranges from 0.9 to 2.2 mg per day. The electroless copper is an industry of worldwide stature with facilities practically in every industrialised nation. The ratio of captive installations (for in-house use) to job plating shop is ~ 3:2; in our country this ratio is higher than ~ 3:1. An estimated copper production in the world by 22 is about 15.75 mtpa and consumption is ~ 14.928 mtpa where as in India it is only around 0.25 and 0.3 mtpa, respectively.

As world population continues to expand, demand for copper tends to increase as well, while remaining sensitive to variances in economic cycles, changes in technology and competition between materials for use in applications. In such a case attention is focused on the technological improvements on pyrometallurgical and hydrometallurgical copper production. Electroless deposition of copper is one such unit operations in hydrometallurgical process. The historic barriers of a lack of end user knowledge of electroless copper and inertia to replace traditional materials of construction are being overcome. The future of electroless copper in our country as well as the world at large is very bright; as the technology of surface coating advances, electroless copper will have its share. Bright, smooth deposit with high plating rate formulation as well as Teflon and particle disperse such as WC and SiC composites are excellent

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example that will allow electroless copper to penetrate new markets.

Above all, void-free and pore free thin coatings with high adhesion to the bulk materials and powder like particles with a wide range of properties will have a special place in Advanced Power Metallurgy in the near future. Such studies and results therefore may open new unique possibilities for obtaining nano-mosaic structures and coatings made of, in particular, refractory metals like W, Mo, Re etc which are of much engineering applications. This nano technology facet of the process under development is of much more advantageous and it is simpler than other expensive and complicated methods and its related production process. Being the fact that it eliminates the difference between the boundary preparation of the modified nanosized materials and the bulk properties of the same materials so as to reveal to the utmost.

The electroless deposition process has several advantages over electroplating such as unlimited throwing power, little or no excess deposit on high points, deposits of excellent chemical and physical properties, excellent uniformity, ability to produce unique catalytic coating and the ability to coat surfaces such as those on the inside of tank cars, non-conductive materials such as ceramics and plastics which would be difficult or impossible to do with conventional electrolytic technique. The electroless copper plating applications are now common in dozen of industries, including chemicals, plastics, printing, mining, textile, papers, food processing machinery, optics and automobiles. The main use of electroless copper includes metallization of ceramics in circuit boards for super computers, LSI packages and sensor materials, printed circuit boards (PCB) metallisation, plating on plastics for auto bumpers, electronics parts in industries, electronics manufacturing, jewellery making and other applications where appropriate conducting, corrosion protection and other surface properties are desired, window layer in heterojunction solar cells, starting material for the synthesis of thin films of copper indium selenide and CIGS films for photovoltaic, filling contact holes and vias in microelectronics devices and delineating semiconductor junctions.

The controlled electrocatalytic deposition of a continuous metallic film on conducting or non-conducting substrate material by the interaction in solutions of a metal salt and chemical reducing agent is known as electroless deposition (Dermott, 1974; Goldie, 1968; Pearlstein and Beills, 1972; Symposium on Electroless Plating, 1959; Mindt, 1971; Riedel, 1991).

This deposition excludes such process as conventional electroplating, which requires externally supplied electrons as reducing agent, uncontrolled precipitation of metals, immersion film produced by displacement reactions due to galvanic difference of potential, thermal decomposition and various types of sputtering and evaporation techniques. Electroless deposition can produce uniform thickness of films of metals (Haruyama and Ohno, 1968; Li and Kohl, 2002; Wurtz, 1844; Chang et al., 1986; Takano and Ishibashi, 1966), alloys (Shinoura and Kamijima, 1993; Bagrowski and Lauriente, 1962; Koiwa et al., 1986; Wolf, 1961; Osaka et al., 1998; Yokoshima et al., 2000) and composites (Paunovic et al., 1993; Osaka et al., 1983; Moradzadeh, 1965; Duncan and Arney, 1984; Okinaka, 1972; Okinaka, 1970; Pearlstein and Weightman, 1974) on both conductive and non-conductive substrate surfaces (Dermott, 1974; Goldie, 1968; Pearlstein and Beills, 1972; Symposium on Electroless Plating, 1959; Chung et al., 1996; Bhattacharya et al., 1999; Naghara et al., 1992).

The different aspects of electroless deposition of copper like substrate surface preparation (Monkowski, 1987; Khilnani, 1988; Kern and Deckert, 1978; Koontz et al., 1959; Bardina, 1988), bah stabilization (Lukes, 1964; Saubestre, 1972; Okinaka et al., 1976; Stokes, 1976; Turner and Okinaka, 1978; Rau, 1978; Paunovic, 198; Schoenberg, 1972), ligand effect (O' Brien, 1986; Dunlop et al., 1966; Schoenberg 1971; Mark et al., 1968; Nuzzi, 1983; Paunovic, 1977; Kondo et al., 199), choice of reducing agents (Ohno, 1991; Pearlstein and Weightman, 1973; Ohno et al., 1985; Hung and Ohno, 199; Ohno et al., 1983; Norkus and Pauliukaite, 1998) and after all the kinetics (El-Raghy and Abo-Salama, 1979; Paunovic, 1968; Schumacher et al., 1985; Feldstein and Lancsek, 1971; Donahue and Yu, 197; Goldie, 1964; Shippey and Donahue, 1973; Molenar et al., 1974; Donahue and Shippey, 1973; Bhatgadde and Mahapatra, 1977; Pyun and Park, 1986; Molenar et al., 1974; Ohno and Haruyama, 1981; Paunovic and Vitkavage, 1979; Donahue, 198; Donahue et al., 198; Jusys and Vaskelis, 1997; Jusys, 1994; Dumesic et al., 1974; Lax and Maughan, 1978; Donahue, 1982; Paunovic, 1985; Donahue, 1974) and mechanism (Schoenberg, 1972; Schoenberg 1971; Paunovic, 1977; Saito, 1965; Sard, 197; Saito and Honma, 1978; Paunovic, 1978; Acosta and Romankiw, 1977; Ambrose, 1973; Bindra and Roldan, 1985; Meerakker, 199; Yang, 1991; Bindra and Tweedie, 1983; Ohno et al., 1985; Dragosavic and Cikovic, 1989; Paunovic, 1987; Paunovic and Stack, 1981; Paunovic and Ting, 1988; Nakahara and Okinaka, 1983; Kim et al., 1984; Choi and Weil, 1981; Paunovic and Zeblisky, 1985; Mishra and Paramguru, 1996, 1997a, 1997b, 1999) have been studied extensively. The mechanism of electroless deposition of copper has been studied by many workers from chemical and electrochemical view points and reviewed in several articles and books (Goldie, 1968; Riedel, 1991; Saubestre, 1959; Donahue, 1972; Modern Electroplating, 1974; Jacobs and Rikken, 1988).

From the work on electrochemical studies by different workers, it is widely accepted that electroless copper plating proceeds along the lines of an electrochemical mechanism as the simultaneous reaction of cathodic

metal deposition and anodic oxidation of reductant according to the mixed potential theory.

The present review is mainly concerned with the correlation of the work of different workers in a single platform for better understanding and to generate better conditions for adherent, smooth and non-porous copper deposition by electroless technique, especially by focusing on substrate surface preparation and kinetics and mechanism of the process.
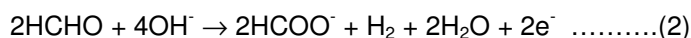
THEORY

Electroless copper deposition by means of the chemical reaction occurs from alkaline solution and therefore cupric ions require a chelating agent. The overall reaction at the copper surface is

$$Cu(L)_2 + 2HCHO + 4OH^- \rightarrow Cu + H_2 + 2H_2O + 2HCOO^- + 2L \qquad \text{.......................(1)}$$
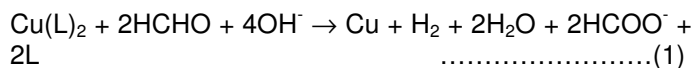
From the electrochemical point of view, this reaction can be considered as two opposite electrode processes or involving two half-cell reactions:
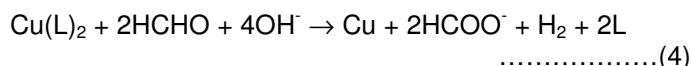
Anodic half cell reaction:

$$2HCHO + 4OH^- \rightarrow 2HCOO^- + H_2 + 2H_2O + 2e^- \text{ ....(2)}$$

Cathodic half cell reaction:

$$Cu(L)_2 + 2e^- \rightarrow Cu + 2L \qquad \text{.......................(3)}$$

Overall reaction:

$$Cu(L)_2 + 2HCHO + 4OH^- \rightarrow Cu + 2HCOO^- + H_2 + 2L \qquad \text{..................(4)}$$

Where, L represents the complexing reagent.

Process mechanism

As mentioned earlier, the electroless deposition of copper can be treated as either electrochemical reduction process or reduction of metal ions by chemical means. In the electrochemical process, the process is pictured as equivalent to corrosion system and consisting of two partial process that is cathodic deposition of metal and anodic oxidation of reductant (Figure 1). This approach explains the necessity of a catalytic surface and the difference in the kinetics of deposition arising from bath chemistry. However, this approach does not provide any explanation for incorporation of the non-metal in the copper deposit.

In case of chemical deposition process, though it does not explain the electrochemical feature of the process but provides an understanding of incorporation of non-metal.

During electroless deposition of copper, the substrate surface preparation, composition of electroless bath, additives for acceleration of the process, bright deposit, kinetics and mechanism of deposition are few important aspects.

Substrate surface preparation (pre-treatment of substrate)

Depending on use and requirements, the electroless deposition of copper is carried out on the desired surface. To obtain better anchoring property as well as surface finish of the deposit, the substrate surface (both metallic and non-metallic) undergoes pretreatments like etching, sensitization and finally activation by $PdCl_2$ solution.

Non-metallic substrate

Electroless deposition of copper can be done smoothly and effectively on the non-metallic substrate surface.

(a) Glass substrate (Schlesinger, 1974; Yoshiki et al., 1994; Yoshiki et al., 1995a; Yoshiki et al., 1995b): Commercially available soda glass and corning 759 glass substrate having surface roughness (R_a) of less than 0.1 μm is first degreased in ethanol and then rinsed thoroughly with deionized water. A solution of 0.5 M zinc acetate in ethanol is sparged in this heated substrate. It is cooled and annealed at 4°C for 2 h in air to relieve stress.

In the activating process, 1.1 mM acidic $PdCl_2$ solution is used as catalysing solution. This solution is prepared from 0.2 g $PdCl_2$ and .5 ml concentrated HCl or NH_3 aq. to pH 2.5. The ZnO /glass substrate is immersed in the above $PdCl_2$ solution without stirring at 25°C, and then washed with the deioniozed water adequately.

(b) PTFE Substrate (Banks, 1979; Muddukrishna and Padma, 1993; Modern Electroplating, 1974; Kondas et al., 1992; Muddkrishna, 1993): PTFE sheets are treated with pyridinium poly (hydrogen flouride), PPHF, in presence of metal powder. The treated substrate material is thoroughly washed with water, dried and then dipped in a solution containing chromic acid, sulphuric acid and hydrofluoric acid for 1 min at 5°C. The substrate material is taken off from the solution and washed adequately with water and dipped into a solution containing sodium hydroxide and sodium dithionate. The substrate is then dipped in HCl (1%) to neutralise any entrained alkali and then thoroughly washed.

The substrate afterwards is dipped in a catalyst solution containing palladous chloride, hydrochloric acid and stannous chloride. The catalyst treatment is carried out under ultrasonic stirring, which produces a uniform layer of palladium on the surface. The surface is treated with
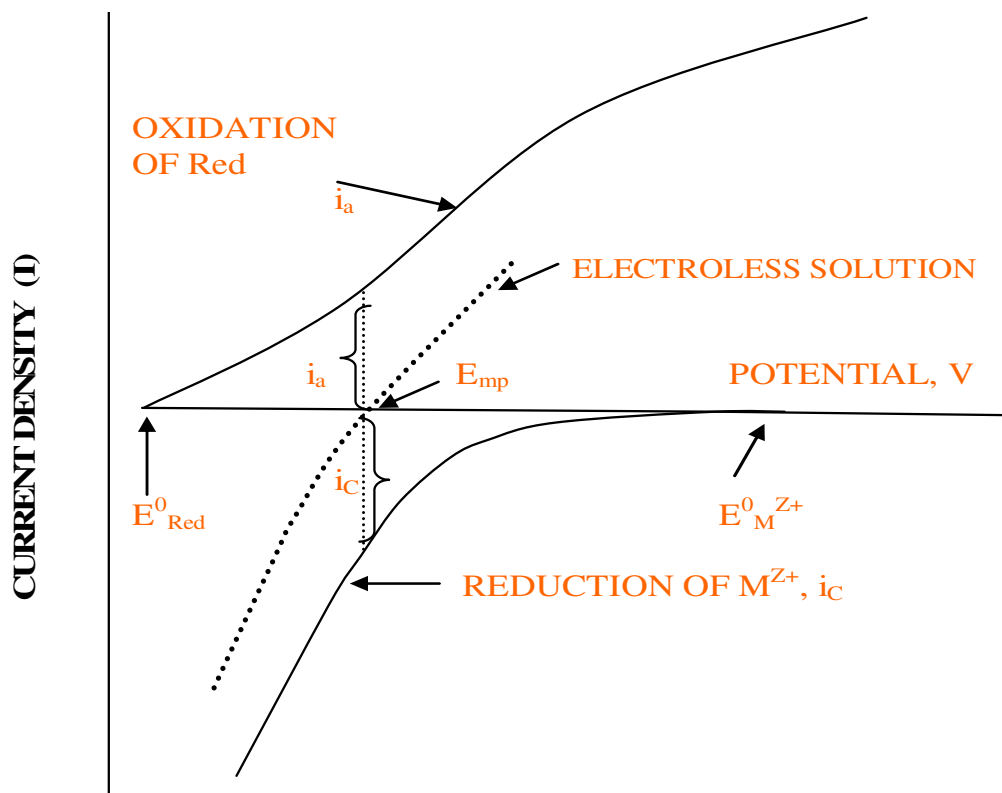
Figure 1. Total and component current - potential curves (i_a + i_c = I_{total}) for the overall reaction.

fluroboric acid to remove any excess metal.

(c) Graphite substrate (Lowenheim, 1974; Schlesinger and Kisel, 1988; Honnma, 1992; Henry, 1989; Caturla et al., 1995; Pai and Rohatgi, 1975; Gopakumar, 1982): Preactivation (surface catalysis) of graphite is accomplished by immersion of graphite for 3 min in an aqueous solution (previously aged for 12 h) of 0.1 M $SnCl_2$ / 0.1 M HCl followed by rinsing in distilled water and immersion for 3 min in an aqueous solution of 0.14 M of $PdCl_2$ / 0.25 M HCl. The soaking time for both solutions is larger than usual for other materials in order to facilitate the access of the reactants to the porosity. The activated piece of graphite are washed with distilled water and then taken for electroless deposition. The same technique is used for activated carbon also.

In some special cases of electroless deposition of copper, the graphite substrate is subjected to a treatment before surface activation in order to modify the surface chemistry; that is, oxidation with an aqueous solution of 0.38 M of $K_2Cr_2O_7$ / 4.5 M of H_2SO_4 for 5 min. It is well known that acid solution of Cr_2O_3 easily etch the surface of graphite. After this treatment, the graphite piece is rinsed with distilled water before activation.

(d) Silicon carbide powder (Chung et al., 1996; Loto, 1987; Cheng et al., 199): The treatment of SiC particulate material consisted of soaking the powder in acetone for about 15 min and with vigorous stirring. After thorough

washing the substrate material is immersed in 68% HNO_3 for 15 min and washed afterwards.

The substrate then undergoes sensitization in an aqueous solution of 1 g/l $SnCl_2$. H_2O and 4 ml/l of 35% HCl for 15 min. Finally after rinsing the particulate material, an aqueous solution of 0.25 g/l of $PdCl_2$ and 2.5 ml/l of 35% HCl is treated for 15 min for activation and then undergoes rinsing and drying at 8 °C, respectively.

(e) Alumina (Schlesinger and Kisel, 1989; Homma et al., 1991; Cohen and Meek, 1976; Cohen et al., 1976; Honma and Komatsuzawa, 1988; Parker, 1981; Severiw et al., 1993; Honma and Mizushima, 1982; Elmore and Hershberger, 1982).

Prior to metallisation, the substrate material is cleaned, etched and enucleated successively in the aqueous solution as follows: First of all, the substrate material is cleanse using surfactant like Amine perfluro alkyl sulfonic acid at 4 °C and at a pH of 6.1. The substrate undergoes rinsing and then etched in dilute HF at 2 °C having pH of 1.1.

After rinsing, the substrate material is put in $SnCl_2$ solution of pH 1.0 at 2 °C and then washed thoroughly. Subsequently, the substrate is immersed in a solution of $AgNO_3$ of pH 1.0 at 2 °C. Finally, the activation of the substance is accomplished in immersing the substrate in $PdCl_2$ solution of pH 2.0 at 2 °C.

Metallic substrate

(a) Ferrite substrate (Bhatgadde et al., 1996): Lithium ferrite substrate having surface roughness <25 A is at first degreased with trichloroethylene. The substrate surface is further roughened by mechanical roughening with alumina abrasive powder up to a surface R_a value of 25 A. Then the surface is rinsed and etched with 4% hydrofluoric acid for 2 min followed by rinsing. The sensitisation is accomplished by immersing the substrate in a hydrochloric acid of .1% by weight, stannous chloride solution of pH 2. for 2 min and then undergoes rinsing. Finally, the substrate is immersed in a hydrochloric acid 0.1% $PdCl_2$ solution of pH 2 for 2 min.
(b) Stainless steel (Henry, 1989; Paunovic and Arndt, 1983; Leyland et al., 1993): All grades of stainless steel can successfully be plated by electroless deposition technique, once the oxide is removed. Stainless steel is having a tendency to form a tenacious oxide film, and, while this oxide is what helps make it resistant to most environments, it presents a problem to finishers. A wood's nickel strike is recommended for 3 series stainless steel because it simultaneously activates the surface while providing a metal displacement coating that helps improve adhesion.

First of all the stainless steel substrate material undergoes soak clean at 17 - 19 F for 5 min and then rinsed. It is then alkaline electrocleaned (cathodic or periodic reverse ending cathodic) at 15 - 18 F for 2 min and then rinsed. After that the stainless steel substrate is treated with a solution of 5% HCl and then 2% H_2SO_4 for 2 min each. And finally undergoes wood's strike for 2 - 5 min.
(c) Copper (El-Raghy and Abo-Salama, 1979; Dragosavic and Cikovic, 1989; Okinaka and Straschild, 1986; Haram and Santhanam, 1992; Oita et al., 1997; Hung, 1985; Ramanauskas, 1997). The established technique for copper electrode preparation for electroless deposition is as follows. Chemically polished electrolytic copper substrate is rubbed with slurry of Vienna lime, an equimolar mixture of $CaCO_3$ and MgO in water. After rinsing the copper substrate is dipped in a solution of 3% HNO_3 for 2 s and followed by activation for 3 s in palladium solution which consists of 0.4 g $PdCl_2$ in 1 ml HCl.

KINETICS AND MECHANISM OF THE PROCESS

Kinetic data on electroless copper deposition from HCHO/EDTA solution are analysed by Schumacher et al. (1985) in terms of formal classical kinetic rate law. The reaction is first order in methylene glycolate and zeroth order in all other reactants. Temperature dependent measurements and isotopic substitution yielded an activation energy of 6.9 kJ/mol and a primary kinetic isotopic effect $k_H/k_D = 5$. Indications are that the rate

determining step involves cleavage of a carbon-hydrogen bond of adsorbed methylene glycolate. The acid dissociation constant of methylene glycolate has been measured between 4 and 7°C. ΔH is found to be 67.2 kJ/mol with ΔS of -25.2 J/(mol.K).

Above all he reaction order for EDTA as ligand is reported as <0.2. Sodium formate addition is suggested to prevent changes in the viscosity and ionic strength of the solution with time and to keep the concentration of product constant.

Paunovic and Vitkavage (1979) attempted to study the electroless copper deposition in the vicinity of mixed potential, E_m. It is stated by him that the determination of the rate of electroless copper deposition is similar to corrosion rate determination. In this connection the applicability of high overvoltage polarisation from E_m is discussed. However, the applicability of low overvoltage polarisation method is highlighted. Steran-Geary equation with and without R_P is measured to determine the rate of electroless plating.

$$i_j = I_{dep} . E_j \tag{5}$$

Where, $E_j = 1^{nj/b}{}_a - 1^{nj/b}c$

And $i_{dep} = b_a . b_c /(2.33 b_a + b_c) . 1/R_p \tag{6}$

Also, Le-Roy equation is utilised is

$$i_{dep} = \sum_{j=1}^{n} (I_j.E_j)/ \sum_{j=1}^{n} (E_j)^2 \tag{7}$$

Rate as calculated with the mixed potential E_{mp} = -68 mV vrs SCE, is 1.59 mg/h/cm^2 gravimetrically or i_{dep} = 1.35 mA/cm^2. This value matches well with the value determined by the above equation.

Weber et al. (1997) have intensively studied the oxidation of formaldehyde in the electroless copper deposition process. Since copper ions are present as EDTA complexes, a catalytic surface is needed to facilitate copper ion reduction. By using electrochemical impedance spectroscopy (Yang, 1991) and surface enhanced spectroscopy, it is found that methanediolate anions, intermediate of the formaldehyde oxidation, acts as such a catalyst. Furthermore, freshly deposited copper exhibits increased catalytic activity toward formaldehyde oxidation. Both effects lead to strong coupling between the anodic and cathodic partial processes. Such a feed back can lead to oscillatory behaviour of the deposition reaction. Scanning tunnel microscopy is also employed to study the deposition rate with high spatial resolution. It is established that the deposition rate fluctuates locally and with time.
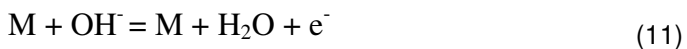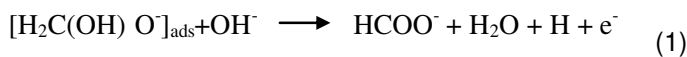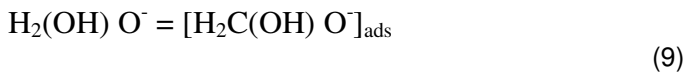
Bindra and Roldan (1985) have discussed the mechanism of electroless deposition of copper in the light of formaldehyde oxidation on different classified metals and thermodynamics of hydrogen evolution reaction. In general it reflects the catalytic activity of the metal for

HCHO oxidation during the process. The mechanism has been studied from cyclic voltamogram. It is reported that metals are classified into three main classes: (i) metals with positive free energy of hydrogen adsorption; (ii) metals with free energy of hydrogen adsorption, close to zero and (iii) metals with negative free energy of hydrogen adsorption.

The stoichiometric numbers has also been calculated by using Allen-Hickling reaction:

$$i = i ([(e^{(n-v)/r} - r\beta) F\eta/RT] - e^{[-(v/v + r\beta)} F\eta/Rt]$$

$$\dots\dots\dots(8)$$

Bindra and Roldan also suggested an ihp mechanism in which the first electron transfer is rate determining. His experimental data is compatible with the following sequence of steps.

$$H_2(OH) O^- = [H_2C(OH) O^-]_{ads}$$

$$(9)$$

$$[H_2C(OH) O^-]_{ads} + OH^- \longrightarrow HCOO^- + H_2O + H + e^-$$

$$(1)$$

$$M + OH^- = M + H_2O + e^-$$

$$(11)$$

$$\overset{|}{\underset{}{}} H$$

$$2H = 2M + H_2$$

$$(12)$$

$$\overset{|}{\underset{M}{}}$$

El-Raghy and Abo-Salama (1979) employed a two-chambered galvanic cell to study the electroless deposition of copper. The concept of Evan's diagram is utilised to know the mixed potential (E_m) and mixed or coupling current (i_m). The electrochemical reaction order is determined from coupling current. Through Evan's diagram, it has been indicated that rate process is increased with increase concentration of any component of the solution but mechanism is different and it is not clear. This technique can be employed to study the other electroless process and with different substrate.
The rate expression suggested is

$$r = k(Cu^{2+})^{.37} (OH^-)^{.254} (HCHO)^{.82} (tart)^{.194} \text{ g.cm}^{-2}. \text{ h}^{-1}$$

$$\dots\dots\dots\dots(13)$$

And order of the electrochemical reaction 'm' is
$$m = \delta logi/\delta logx_y$$

Where:

i = coupling current,
x = concentration of one component,

y = concentration of other component.

The Wagner - Traud (1938) theory of mixed potential concept has been utilised by Bindra which mention that the partial faradic process that is the anodic and cathodic reactions involved are independent of each other but depends on the electrode potential.

But controversy raised by Raghy and Donahaque that the partial reactions, are not entirely independent of each other. The technique of Makrides (196) of corrosion of iron in H_2SO_4, is used to study the partial reactions and comments that the cathodic partial reaction is entirely diffusion controlled and the anodic partial reaction totally is activation controlled. The measurement is made using rotating disc electrode and the electrochemical expression for E_{mp} used is

$$E_{mp} = E_R - b_R \ln n_R + k_a - b_R \ln c^\infty_R + b_a/R \ln B'_M2 + b_R \ln c_{M+}$$

$$\dots\dots\dots\dots (14)$$

Ohno et al. (1985) have tried to explain the mechanism of the process by catalytic activity of the metals for the anodic oxidation of different reductant by the potentials at a reference current density and at various temperatures. A catalytic activity series thus obtained can be utilised for choosing a suitable reductant for metal deposition. Some co-relation is observed between the catalytic activity and the apparent activation energy.

Different reaction mechanism has been proposed for hydrogen evolution reaction during electroless plating such as: (a) proton discharge mechanism, (b) the hydroxide mechanism, (c) the hydroxide ion mechanism and (d) atomic hydrogen mechanism.

The inter-dependence of partial reactions in electroless plating process has been studied by Bindra (1985), Bindra and Tweedie (1983) and Bindra and Roldan (1987). It has been shown that the overall mechanism of an electroless plating process can be determined by observing the behaviour of the mixed potential as a function of agitation, the concentration of metal ions or the concentration of reducing agent, if the partial reactions are either diffusion or electrochemical control.

The overall mechanism has been considered when the partial reactions are either under diffusion control or electrochemical control. It is suggested that the formaldehyde reaction is electrochemical control while the metal deposition partial reaction is diffusion controlled. The analysis leads to kinetic parameters presented in Table 1.

Gottesfeld et al. (1986) had concepted the electroless copper process from different angle and his study was supported by RBS and AES. It reveals the fact that Pd catalyst migration takes place from the deposit substrate to the deposit solution interface but negligible whether wet or evaporated Pd catalyst is employed. It is suggested that H_2 rather than H_2O be expected to be final product of H_2CO electroxidation at copper at potentials as

**Table 1.** Kinetic parameters obtained in different condition.

Method	Electrolyte	Slope (mV)	Transfer co-efficient
$\delta E_{mp}/\delta \log$	Complete bath	14	0.34
$\delta E_{mp}/\delta \log [HCHO]$	Complete bath	21	0.33
$\delta E_{mp}/\delta \log [CuSO_4]$	Complete bath	188	0.37
$\delta E_{mp}/\delta \log i_R$ (galvanostatic)	Anolyte	185	0.38
$\delta E_{mp}/\delta \log i_R$ (potentiostatic)	Anolyte	11	0.64
$\delta E_{mp}/\delta \log i_m$ (potentiostatic)	Anolyte	115	0.61
$\delta E_{mp}/\delta \log i_m$ (galvanostatic)	Complete bath	-3 ± 5	0.43
$\delta E_{mp}/\delta \log i_m$ (potentiostatic)	Catholyte	-155	0.42

high as +.4 V vrs. RHE, provided the activation energy for recombinative hydrogen desorption from the copper surface is less than 1 Kcal/mole.

During electroxidation the methylene glycolate anion is likely to be absorbed from solution not through a 'O' atom but rather with C-H bonds adjacent to copper surface. The two reasons are being (a) the negative charge on copper expected at this pH and metal solution, which would tend to orient the negative charged 'O' atom away from the surface and (b) hydrophobic interactions of the C-H side of the molecule. The resulting conclusion is that the form in which formaldehyde actually exists in an aqueous solution that is the methylene glycolate anion formed by

$$H_2CO + OH^- [H_2C(OH)O^-] \longrightarrow \qquad (15)$$
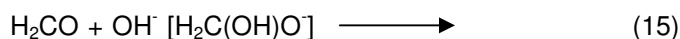
is a key factor in the kinetics of its electroxidation. His valid reasonable argument leads to the following schematic electro dehydrogenation of an adsorbed methylene glycolate anion.

$$\dots\dots\dots\dots\dots\dots\dots(16)$$
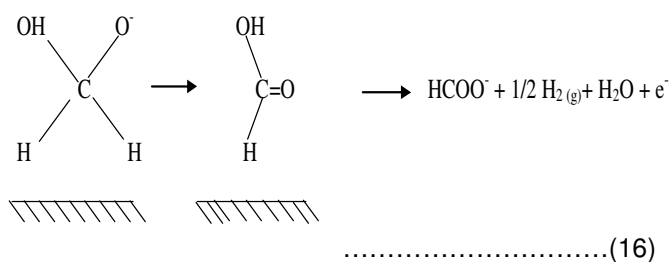
The effect of varying concentration of the electrolytes of the electroless bath on the kinetics has been analyzed by Molenar et al. (1974a, b). At a higher concentration range of cupric ions, the rate of electroless plating is independent of NaOH and HCHO concentration. But at lower formaldehyde and hydroxide concentration, the authors suggests that the copper deposition is determined by diffusion of hydrated formaldehyde anions and varying cupric ions has no effect on the rate of electroless plating. This data have been employed in the empirical rate equation of Shippey and Donahue (1973).

$$r = \Delta Cu/\Delta t = k [Cu]^a [OH^-]^b [HCHO]^c [EDTA]^d e^{E(T-323)/323 RT}$$
$$\dots\dots\dots(17)$$

The cathodic slope of 17 mV is in good agreement with values found for electrolytic deposition in sulphuric acid solution. At low formaldehyde and hydroxide concentration the authors conclude that the diffusion of the methylene glycol anions to reaction zone is the determining factor of deposition reaction.

Ohno (1991), Ohno and Haruyama (1981) and Ohno et al. (1985) has described the electrochemical aspects of electroless plating in four sections: (a) electrochemical polarisation behaviour using mixed potential theory; (b) catalytic aspects of electroless plating; (c) mechanism of anodic oxidation of reductant; (d) methods for determining the rate of electroless plating.

It is stressed that the electrochemical polarisation studies in an electroless plating bath is a powerful method for assessing the adaptability of the bath and for obtaining mechanistic information, although the anodic and cathodic reactions are more or less independent when occur simultaneously. Catalytic aspects of electroless plating are discussed on the basis of the polarization curve for the anodic oxidation of reductant. The mechanism of anodic oxidation of the reductants is discussed on the basis of computer simulation of the current density-potential curve assuming several reaction schemes. Attention is focused especially on the occurrence of the volcano-shaped polarisation curve. It is established that the polarisation resistance is inversely proportional to the rate of electroless plating.

The effect of pH on the kinetics and mechanism of the process cannot be overlooked. Duffy, Pearson and Paunovic (1983) have studied the effect from electrochemical and spectroscopic viewpoint. They have considered the effect of pH on electroless copper deposition in two ways:

(i) First and primary pH effect is, the OH^- ions are reactant in the overall and the partial anodic reaction and affect these reaction in a direct way.

Table 2. Expected dependence of E_m and i_m on [Cu$^{2]}$, [HCHO] and [OH$^-$].

S/No.	Function	Situations (i), (ii), (iii) and (iv)			
		Cathodic linear-anodic limiting current	Cathodic Tafel-anodic limiting current	Both anodic - cathodic Tafel	Cathodic Limiting current -anodic Tafel
1.	E_m	$E_c + \{(2.33RT)/z_cF\}\log[Cu^{2+}]$	$\{(2.332RT)/F\}\log\{A_ck_{cf}[Cu^{2+}]d_a\}/(A_aD_a[HCHO])$	$\{(2.33RT)/F\}\log(\{A_ck_{cf}[Cu^{2+}]\}/\{A_ak_{cf}[HCHO][OH^-]\})$	$\{(2.33RT)/F\}\log(\{A_cD_c[Cu^{2+}]\}/\{A_ak_{af}[HCHO][OH^-]d_c\})$
2.	i_m	$2FA_aD_a[HCHO]/d_a$	$2FA_aD_a[HCHO]/d_a$	$2F(k_{af}A_ak_{cf}A_c)([Cu^{2+}][HCHO][OH^-]^{1/2})$	$Z_cFA_cn_cD_c[Cu^{2+}]/d_c$
3.	$\delta E_m/\delta\log[Cu^{2+}]$	0.03	0.118	0.059	.118
4.	$\delta E_m/\delta\log[HCHO]$	0.0	-0.118	-0.059	-.118
5.	$\delta E_m/\delta\log[OH^-]$	0.0	0.0	-0.059	-.118
6.	$\delta i_m/\delta\log[Cu^{2+}]$	0.0	0.0	0.5	1.
7.	$\delta i_m/\delta\log[HCHO]$	1.0	1.0	0.5	.
8.	$\delta i_m/\delta\log[OH^-]$	0.0	0.0	0.5	.

(ii) Secondly, in the secondary pH effect, it influences various phenomena involved in metal solution interphase, like (a) potential of zero charge, (b) adsorption, (c) structure of Cu species, and (d) the ionic strength of the solution.

In their electrochemical approach, the rest potential and the transfer coefficient of partial reactions have been considered and spectroscopic data gives insight into the composition of the adsorption film.

These previous investigations on kinetics and mechanism of electroless copper deposition help the present authors (Mishra and Paramguru, 1996, 1997a, b, 1999) to study the process mechanism extensively in a semi-quantitative manner employing Butler-Volmer equation. It is established that the mechanism changes from anodic to cathodic control as well as from diffusion to activation control depending on the concentration of Cu^{2+} and HCHO. Since the reactions are governed by mixed potential theory, Stern-Geary equation and Wagner-Traud theory of mixed potential have been employed to explain the process. The position of mixed potential, E_m,

in the polarisation curve classified four different situations at varying copper ion and formaldehyde concentration as shown in Table 2.

Deposition rates reported by different authors (Ohno) under different conditions may be presented as support to these studies. The data are presented in Figure 3 with hatching indicating the prevalence of the four cases. It is remarkable that a co-relation exists between the relevant parameters reported at serials 6 and 7 of the Table 2 and in Figure 2 for the four cases examined.

From our study it is worth to present the equations along with the expected dependence of E_m and i_m on the concentrations of Cu^{2+}, HCHO and OH$^-$.

ALTERNATIVE ELECTROLESS BATH WITH REGARDS TO COMPLEXING AGENTS AND REDUCTANTS

Kondo et al. (1991) have studied extensively the effects of addition of various ligands like EDTA, HPA, HEA, NTA, TIPA and TEA on the electroless

copper deposition rate. TEA is fund to be the most effective ligand for increasing the electroless copper deposition rate. At lower TEA concentrations, the deposition is increased until it peaked. After peaking, it decreased with increasing concentrations. The maximum rate is over 2 fold faster than the current rate observed in the EDTA system. A new deposition model (Figure 3) is also suggested by Kondo to derive the adsorption kinetics and to understand the effect of excess ligands. It is also presumed that all adsorption process is equilibrated and follows Langmuir isotherms. In Figure 3c, the fractional surface coverage of active Cu (II)-TEA, θ_3, is expressed as:

$$\theta_3 = \{(K_1.\ C_{xl})/(1+K_1.\ C_{xl})\}.\{(K_3.\ C_c)/(1+K_3.\ C_c)\}.\{1/(1+K_i.\ C_{xl})\} \quad (18)$$

Where C_{xl} and C_c are the concentration of excess TEA and Cu(II)-TEA respectively: K_1 and K_2 are the adsorption equilibrium constant for excess TEA onto the reactive surface and onto the adsorbed Cu(II)-TEA, respectively: and K_3 is the
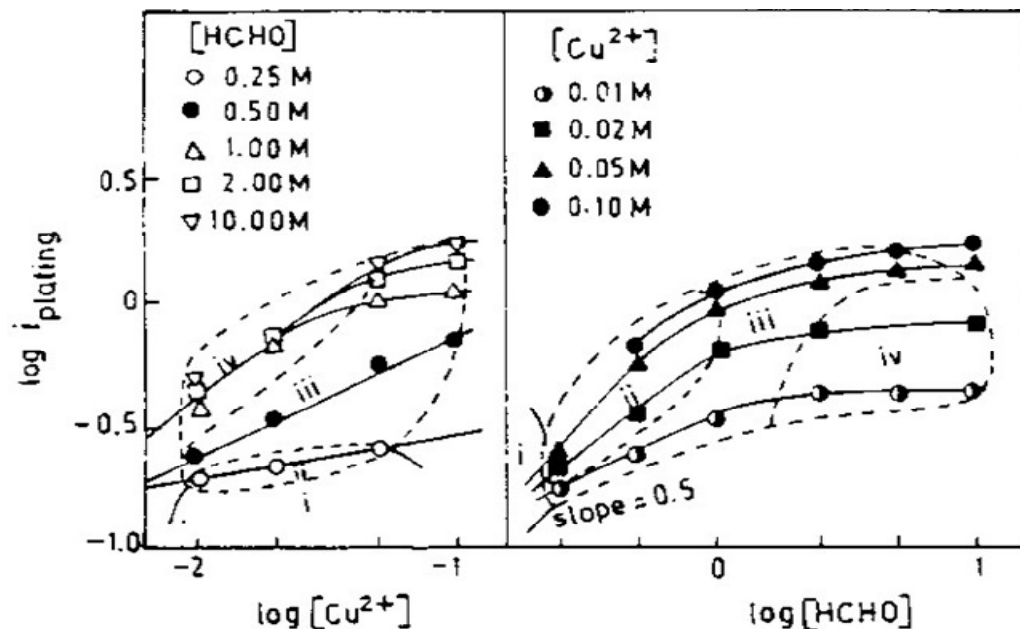
Figure 2. Plot of log I$_{plating}$ vs. log [Cu^{2+}] and [HCHO] obtained from results of Ohno (1991). Regions of validity of different mechanisms (case (i) through (iv) are also shown in the Figure.
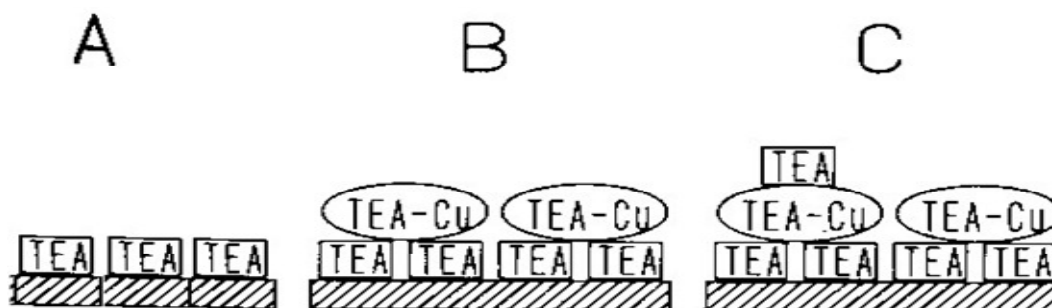

Figure 3. Deposition model on the reactive surface.

Cu(II)-TEA adsorption equilibrium constant onto the adsorbed TEA.

The mechanism of electroless copper deposition from a new iminodiacetate (IDA) bath is studied by Ohno (1976) and found to be fully explained by the mixed potential theory. The bath consists of aqueous solutions of cupric sulphate, iminodiacetic acid, formaldehyde and sodium hydroxide. With increasing pH, both the oxidation of formaldehyde and the reduction of the Cu-complex are promoted and hence the deposition rate is increased. From the study of the adsorption spectra of the electroless bath in presence and absence of IDA, it is highly probable that the main reaction complex formation should be

$$[Cu(H_2O)_4]^{2+} + 2 \; IDA \longrightarrow [Cu(IDA)_2]^{2+} + 4H_2O \tag{19}$$

But there exists also various complex ions with various Cu^{2+} to IDA ratios.

At optimum condition, the rate of deposition from the IDA bath is comparable with that from the EDTA bath. However, the latitude of the IDA bath for pH change is rather wide and the bath gives a thicker deposit film compared with that from the EDTA bath (Table 4).

Gloxylic acid as a new alternative reducing agent for electroless copper deposition is suggested by Honma and Kobayashi (Honma and Kobayashi, 1994). From their study it is suggested that plating rates and bath stability are superior to that of formaldehyde bath under standard conditions. The morphology of the deposited copper film is not greatly affected by EDTA concentration and mechanical properties (ductility) of deposited films are obtained. The rate of Cannizaro reaction with glyoxylate ions is faster than with formaldehyde, but

Table 3. The position of mixed potential, E_m, in the polarisation curve classified four different situations at varying copper ion and formaldehyde concentration.

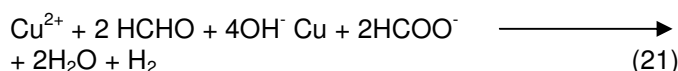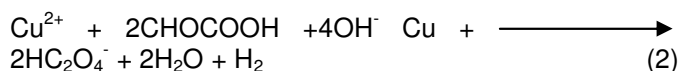| E_m lies on	Mechanism	Solution condition
(i) Cathodic linear - anodic limiting current	Anodic diffusion control	Very low HCHO and moderate Cu^2
(ii) Cathodic Tafel - anodic limiting current	Anodic diffusion control	Very low HCHO
(iii) Both anodic and cathodic Tafel	Activation control	Moderate to high HCHO and Cu^2
(iv) Cathodic limiting current and anodic Tafel	Cathodic diffusion control	Low Cu^{2+} and high HCHO

Table 4. Comparison of deposit rates from IDA and EDTA bath.

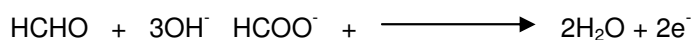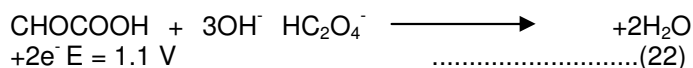|		IDA bath (present result)	EDTA bath (Ref. 6)
(1) I-E curve of Cu complex	iE_{rest}	0.029 mA. cm^{-2} -0.29 V (vs. SCE)	0.034 mA. cm^{-2} -0.47 V (vs. SCE)
(2) I-E curve of HCHO	iE_{rest}	0.16 mA. cm^{-2} -0.9 V (vs. SCE)	0.44 mA. cm^{-2} -1.1 V (vs. SCE)
Estimated from (1) + (2)	$i_{dep}E_{mp}$	1.5 mA. cm^{-2} -0.64 V (vs. SCE)	1.9 mA. cm^{-2} -0 .65 V (vs. SCE)
Estimated from (1) and E_{mp} (expt.)	$i_{dep}E_{mp}$ (expt)	1.2 mA. cm^{-2} -0.63 V (vs. SCE)	1.8 mA. cm^{-2} -0.66 V (vs. SCE)
Determined gravimetry	i_{dep}	1.15 mA. cm^{-2}	1.8 mA. cm^{-2}

could be reduced by 1 to 4% using KOH instead of NaOH. It is confirmed that the uniformity of the hole all coverage is superior to that of the formaldehyde bath. Glyoxylate ions in the plating bath have no vapor pressure and showed good reducing power in the electroless copper plating. Therefore, glyoxylic acid can replace traditional formaldehyde, and eliminate health environmental problems resulting from generation of obnoxious fumes.

The overall reaction of glyoxylic acid bath corresponds to that of formaldehyde bath. Reduction potential of glyoxylic acid is similar to that of formaldehyde.

Overall reaction:

$$Cu^{2+} + 2CHOCOOH + 4OH^- \rightarrow Cu + 2HC_2O_4^- + 2H_2O + H_2 \qquad (2)$$

$$Cu^{2+} + 2 HCHO + 4OH^- \rightarrow Cu + 2HCOO^- + 2H_2O + H_2 \qquad (21)$$

Standard redox potential:

$$CHOCOOH + 3OH^- \rightarrow HC_2O_4^- + 2H_2O + 2e^- \quad E = 1.1 \text{ V} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(22)$$

$$HCHO + 3OH^- \rightarrow HCOO^- + 2H_2O + 2e^-$$

$$E = 1.7 \text{ V} \qquad (23)$$

Conclusion

(1) Pretreatment of substrate material differs from substrate to substrate and careful treatment leads to better anchoring property and surface finish for electroless copper deposit.

(2) Whether the substrate is conducting or non-conducting, it undergoes palladium coating for making the surface catalytic before electroless deposition. The mechanism being that Pd catalyst migration takes place from the deposit substrate to the deposit solution interface but negligible whether wet or evaporated Pd catalyst is employed.

(3) Electroless copper deposition is an electrochemical phenomenon and anodic and cathodic half-cell partial reactions can be studied independently using current-voltage polarisation curves.

(4) The kinetics and mechanism of electroless deposition of copper can be studied from electrochemical angle using partial anodic and cathoidic half cell reactions.

(5) Glyoxylic acid is a better substitute for formaldehyde as a reductant, being environmentally benign and having close electrode potential to that of formaldehyde.

(6) Triethanolamine proves to be a better complexing

agent as it enhances the deposition rate and gives a thicker bright deposit of copper.

ACKNOWLEDGMENTS

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