RECENT ADVANCES IN ELECTROLESS COPPER DEPOSITION – A REVIEW

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Abstract: *This article reviews the recent advances in electroless copper plating and discusses the role of complexing agents, reducing agents and the role of additives in the rate of deposition. Environmental concerns have led to interest in developing cyanide and EDTA-free methanesulphonate baths for electroless deposition of copper. Eco- friendly polyhydroxy compounds has found more importance as an complexing agent replacing EDTA and other common chelators. The role of different reducing agent in the electroless copper deposition has been studied and summarised. The effect of bath operating conditions (temperature, pH and agitation) and bath additives on plating rate, bath stability, morphology and etching rate of the coating has been discussed. Lone pair of electron bearing elements like Nitrogen and Sulphur containing organic compounds are generally used as additives. The additives were found to modify the crystal structure with the production of small grain size, dense, tightly adherent and etching resistant copper deposits.*

Key words*: Chelators, additives, EDTA, etching, adherent.*

INTRODUCTION

Electroless plating is an autocatalytic process more useful than electroplating for the deposition of metal coatings and films because of improvements in solution stability, possibility of producing coatings with uniform thickness, capability of depositing material even in deep recesses, bores, blind holes, high selectivity, possibility of producing very thin layers, excellent step coverage, good filling capacity and absence of need for electrical contacting of wafers during deposition. The controlled electroless plating process was accidently discovered by Brenner and Riddell in 1946, when they tried to electroplate Ni-W alloy on the inner side of a steel tube using a citrate bath. They modified the plating bath using several reducing agents including sodium hypophosphite. Based on its analogy with the electroplating process, William Blum coined the term 'Electroless plating' for this process.

Electroless plating is a technique of depositing a noble metal from its salt solution on a catalytically active surface of a less noble metal by employing a suitable reducing agent without using electrical energy. The reducing agent supplies the electron for reduction of metallic ion into the metal which is deposited over the substrate surface giving a uniform thin coating. These electroless plated coatings can be as thin as 0.0005 and up to 0.010 inch.

Metal ion + Reducing agent → Metal + Oxidized product [1]

(Deposited)

COPPER AS PLATING METAL

The industrial use of copper started in the late 18th century from the discovery and developments in electricity and magnetism by such scientists as Ampere, Faraday and Ohm. Electroless copper coatings provide protection for common metal surface exposed to corrosion and wear. Electroless copper, as an engineering coating, is used in many industrial applications in aerospace automotive computers, electronics, food processing, hydraulics machinery, nuclear engineering, oil petrochemicals, plastics, power transmission, printing, pump valves, textile [1-2] etc.

Electroless copper coating methods are used in micro technology. Electroless copper and its alloys are being increasingly used as materials for interconnects and packing applications for ultra-large-scale integration (ULSI) [3-6] due to their low resistivity and high electro migration resistance [7]

In 1950, Procell recognized the use of alkylsulphonic acids for electroplating applications. He found that alkylsulphonic acids, having between one and five carbon atoms in the alkyl group, formed water soluble salts of various metals. This system only gained commercial acceptability during the early 1980’s and methanesulphonic acid became a potential electrolyte for use in various metal coating applications.

Methanesulphonic acid is a colourless liquid with the chemical formula CH_3SO_3H. It is the simplest of the alkylsulphonic acids. Methanesulphonic acid is a slightly yellow transparent liquid, which is soluble in water and little soluble in benzene and methylbenzene, but it is insoluble in paraffins. Salts and esters of methanesulphonic acid are known as mesylates. MSA is a strong electrolyte and its conductivity in water is similar to other strong acids such as sulphuric or hydrochloric and higher than that of other organic acids. It is also considered to be natural product and is part of the natural sulphurcycle [8].

MSA is considered to be a ‘green’ solvent/chemical because of the following reasons:

(i) It is odorless and does not generate toxic gas fumes, and is thus very safe to handle.

(ii) It is readily biodegradable, forming sulphate and CO_2.

(iii) It is recyclable because of its excellent solubility in water.

(iv) Its high strength makes it a good catalyst of many organic transformations.

(v) It is as catalyst, and solvent for many condensation and rearrangement reactions [9-11].

In addition to the above listed advantages, MSA’s superiority over other bath liquid arises also from its excellent metal salt solubility, excellent conductivity, ease of effluent treatment, stability and bio-degradability [12]. It can be operated at room temperature [13]. Additions of small amounts of MSA have been reported to produce uniform and high quality coatings [14].

ROLE OF COMPLEXING AGENTS

De Minjer and Brenner studied the relationship between ligand concentration and the plating rate. Small additions of the complexing agent are accompanied by an increase in plating rate. Complexing agents for electroless copper baths have almost always fallen into one of the following groups of compounds: EDTA, triethanolamine, tartarate, quadral, trisodium citrate, malic acid and lactic acid [15-17].

In 1970’s EDTA salts were widely used for complexing in electroless copper solution. Because it is not only very weakly adsorbed on copper [18-20] surface, but also has excellent chelating properties over a wide *p*H range. The EDTA bath shows dual chelating property (i.e.) it avoids cupric hydroxide precipitation and maintains the stability of electroless plating. However EDTA is not very bio-degradable, forms complexes with heavy metals increases the total nitrogen content of waste water and produces serious pollution problems in waste water [21-22].

The use of Triethanolamine (TEA) as a chelating agent has been reported to result in plating rate about 20 times higher than when using EDTA [23-24]. The SEM analysis of copper deposition with TEA as chelant showed shrinkage in the grain while grain size was more uniform with EDTA.

Tartrate is used for low plating rate and low temperature application and involves easy waste treatment options. However, it is not applicable in faster plating systems.

Polyhydroxylic compounds have been gaining importance as chelating agents in electroless plating because they are bio-degradable [25]. Polyhydroxy compounds (polyols), which were reported in the late 20th century to form chelates with Cu(II) ions in alkaline medium are potential replacements to EDTA. They are well suited for copper electroless plating because they form stable complexes with copper (II) ions in alkaline solutions. This minimizes the amount of free Cu(II) in the solution, and thus prevents the precipitation of $Cu(OH)_2$ and improves quality of copper plating.

Many natural polyhydroxylic compounds like glycerol, xylitol, saccharose, alditol, erythritol, adonitol, D-mannitol, D-sorbitol, maltitol, lacticol and dulicitol have been proposed as environmentally friendly chelating agents for alkaline electroless plating. These natural polyhydroxylic chelators are stable and possess good chelating properties for Cu (II) ion in alkaline medium [26].Among the polyhydroxylic alcohols only glycerol has been widely used as a Cu(II) ligand in electroless copper plating solutions [27-30].

Alditols (saturated polyhydroxylic alcohols) could provide alternatives to EDTA in electroless copper plating processes. They form very stable complexes withCu(II) ions in alkaline solutions that result in free Cu(II) concentrations low enough to prevent the precipitation of $Cu(OH)_2$, but do not form metal complexes under the near-neutral pH conditions found in waste-water treat-ment processes and natural waters [31-33]. In addition, these natural polyhydroxylic compounds are easily biodegradable. Therefore, the use of alditols as environmentally friendly ligands for electroless copper baths is promising.

Electroless copper plating solutions containing the chelators such as xylitol, D-mannitol and D-sorbitol are stable and under optimal conditions, copper coatings up to 3 µm thick can be obtained in 1 h at ambient temperatures [34-35]. Xylitol forms three mononuclear copper (II) hydroxyl complexes at high ligand-to-metal ratios and under optimal operating conditions a plating rate of 2.5-3 µm/h has been observed.

Saccharose is another ecofriendly chelating agent that has been studied by [36]. Saccharose forms sufficiently stable complexes with Cu(II) ion in alkaline solution [37]. The plating starts at *p*H value above 12, and maximum plating rate is observed at *p*H of 12.75, the plating rate is reduced at higher *p*H values. A plating rate of 3 µm/h has been observed under optimal condition.

ROLE OF REDUCING AGENTS

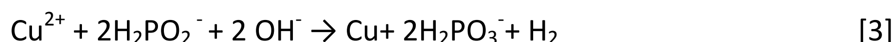
A good reducing agent for electroless copper baths should be capable of completely reducing divalent copper to metallic copper and not to intermediate cuprous oxide. Traditional electroless copper plating solutions often use formaldehyde as the reducing agent because of its low cost and the high quality of the deposit [38]. When formaldehyde is used as the reducing agent in the plating bath, the electroless copper deposition can be considered to consist of the following reaction.

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

However, when formaldehyde is used as the reductant, the plating solution should have a high pH value [39]. Thus, some plating materials cannot be used along with formaldehyde because of the alkaline corrosion of the electrolyte. In addition to that, formaldehyde is a volatile toxic compound and the plating solution is easily decomposed. Therefore, non-formaldehyde electroless copper plating is preferred.

Currently, glyoxylic acid [40], hypophosphite [41-44], sodium bisulfate ($NaHSO_3$) and the sodiumthiosulfatepentahydrate($Na_2S_2O_3$,$5H_2O$) [45], Co(II) [46], Fe(II) [47], borane dimethylamine complex [48-49], etc, have been developed as substitutes for formaldehyde.

Among these, the plating process using hypophosphite as the reductant has attracted considerable attention due to its low price, good bath stability, and relatively easy to control plating conditions. It may replace the formaldehyde electroless copper plating and may be applied in industries[50].The overall electroless copper plating reaction using hypophosphite as the reducing agent is given

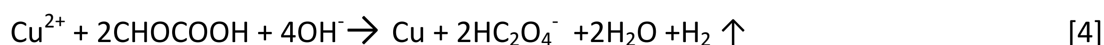


$Cu^{2+} + 2H_2PO_2^{-} + 2OH^{-} \rightarrow Cu + 2H_2PO_3^{-} + H_2$ [3]

However, the inherent drawback for using hypophosphite as the reducing agent is the weak catalytic activity for the oxidation of hypophosphite on copper. While the initial substrate surface is palladium-activated, once it is coated with copper, the reaction slows. One way to compensate for the poor catalytic activity of copper is to add nickel ions to the solution [51-52]. The codeposited nickel in the copper deposit serves to catalyze the oxidation of hypophosphite, thus increasing the overall deposition rate [53].

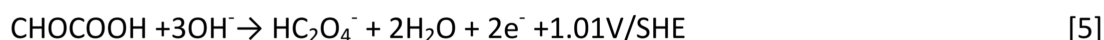
Glyoxylic acid as an alternative reducing agent for electroless copper plating was investigated. Plating rates and bath stability were superior to that of the formaldehyde bath under standard conditions [54]. The morphologies of deposited copper film were not greatly

affected by ethylenediaminetetraacetic acid concentration, and mechanical properties (for instance, the ductility) of deposited films were obtained. The rate of the Cannizzaro reaction with glyoxylate ions was faster than with formaldehyde, but could be reduced by 10 to 40% using KOH instead of NaOH. It was confirmed that the uniformity of hole wall coverage was superior to that of the formaldehyde bath. Glyoxylate ions in the plating bath have no vapor pressure [55] and showed good reducing power in the electroless copper plating. Therefore, glyoxylic acid can replace formaldehyde, and eliminate health and environmental problems resulting from generation of obnoxious fumes [56-57]. The overall reaction is,



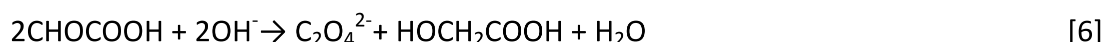
$$Cu^{2+} + 2CHOCOOH + 4OH^- \rightarrow Cu + 2HC_2O_4^- + 2H_2O + H_2 \uparrow \quad [4]$$

Standard redox potential



$$CHOCOOH + 3OH^- \rightarrow HC_2O_4^- + 2H_2O + 2e^- \; +1.01V/SHE \quad [5]$$

This reaction is commonly accompanied by the Cannizzaro reaction,



$$2CHOCOOH + 2OH^- \rightarrow C_2O_4^{2-} + HOCH_2COOH + H_2O \quad [6]$$

A number of workers have investigated the electroless deposition of copper using Dimethylamine borane(DMAB) as the reducing agent. DMAB has a number of advantages over formaldehydebased plating baths. It does not produce toxic fumes and it can be run at a lower pH. DMAB has been used to deposit copper on to electroless nickel, palladium activated plastic, copper substrates [58] and tin/palladium activated epoxy [59], with deposition rates of approximately 2.3µm/hr and 4 µm/hr, respectively.

Other reducing agents have been investigated such as phosphinate, hydrazine [60], aminoborane and phenylhydrazine, but their applications are limited, because bath stability and deposited film properties are not optimal [61-62].

ROLE OF ADDITIVES

A persistent problem in the use of electroless copper baths has been their tendency to decompose spontaneously. Forthese reasons, many organic additives have been proposed to serve as stabilizers.Presence of additives in electroless copper bath may alter the physical and mechanical properties of plate during the deposition [63-66]. They could behave as one or more of the following during the electroless plating process.

(i) Carriers
(ii) Levelers
(iii) Brighteners

(iv) Wetters

(i) Carriers help increase throwing power into holes and other surface features. They adsorb on the cathode surface during plating to form a monolayer film. They form a barrier to diffusion of Cu^{2+} to the surface and suppress plating rate. E.g., Polyethers or polyoxyethers

(ii) Levelers improve plating thickness uniformity. They adsorb strongly on the surface at high current density regions. This lowers the plating rate at corners and projections and levels the plated layer. E.g., Organic nitrogen compounds, amines, amide surfactants

(iii) Brighteners control deposit brightness and hardness. They attach to the copper metal ions during plating and facilitate charge transfer at the electrode. Brighteners accelerate plating rates and also control grain structure and deposit characteristics. E.g., Sulphur containing compounds

(iv) Wetters decrease surface tension in solution. Surfactants lower the surface tension of the plating solution and thus, allow better wetting of the electrolyte at the electrode.

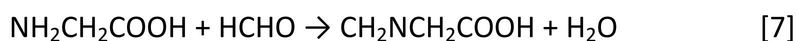
The use of inorganic additives as stabilizer has been reviewed by Bielinski and Kaminski (1987), over two hundred papers and patents had been published on the effects of large number of these stabilizers on the plating solution. Compounds having planar and other structures with lone pairs of electrons such as sulphur and nitrogen containing organic compounds have been proposed to serve as stabilizers [67]: pyridine, cytosine, thiourea, guanidinehydrochloride, 2-mercaptobenzothiozole (2MBT), KCN, potassium ethylxanthogenate, benzotriazole, polyethyleneglycol (PEG), dithiocarbamate [68-69] and 2,2'-dipyridyl [70-71] etc.

It has been found that all the organic additives studied except thiourea not only stabilize electroless copper baths but also enhance theplating rate from 1.1 to 1.8 mg/(cm^2h) in the tartarate bath at 30 jC and from 5.4 to 10.5 mg/(cm^2h) in the EDTA bath at 50 jC. Mild air agitation increases the bath stability 20 times that of bath without aeration. The additives were found to modify the crystal structure with the production of small grain size, dense, tightly adherent and etching resistant copper deposit [72].Thiourea derivatives acted as stabilizers and retarded the rate of electroless copper deposition through their effective adsorption on metal surface.

Cyanide, not only stabilizes the plating bath but enhances deposit ductility. The mechanism is likely to be that of competitive adsorption of the strongly adsorbed CN^- ion and the

intermediate adsorbed hydrogen radical, thus precluding hydrogen entrapment and embrittlement. Addition of polyethylene glycol to electroless copper baths generally improves ductility, particularly at higher molecular weights [73].

Glycine has been observed to decrease the plating rate and increase ductility and tensile strength for copper deposits, although the proposed mechanism is somewhat different than described above [74]. Glycine and formaldehyde form a condensation product according to the following reversible equilibrium:



$$NH_2CH_2COOH + HCHO \rightarrow CH_2NCH_2COOH + H_2O \quad [7]$$

Therefore, increasing the glycine concentration tends to lower the free formaldehyde concentration, which in turn reduces the plating rate and improves the deposit metallurgy. In addition to the above homogeneous reaction, glycine is also a complexant for cuprous ion and may function as a stabilizer in much the same fashion as CN-, although the stability constant is lower for the glycine complex.

Guanine and Adenine have been shown to accelerate plating in electroless copper deposition, and also suppress oxidation and passivation of metallic copper in alkaline solution. The accelerating property is due to the N atom, π electron density and π electron adsorbed molecules. Sulphur compounds have also been used in conjugation with nitrogen compounds like nitrile [75-78].

Ammonia acts as an effective accelerating agent in electroless copper plating. The electroless deposition rate has been found to decrease with the addition of 2,2’-dipyridyl to the plating solution and the colour of the deposit changes from dark brown to semi-bright. The deposit was also found to have smaller crystals and higher (111) plane orientation. 2,2’-dipyridyl has been reported to improve the micro structure and properties in hypophosphite bath [79-80]. The deposits became uniform and compact because 2,2’-dipyridyl inhibited catalytic oxidation, thus reducing the deposition rate and making the deposit fine in structure [81-83]. Sodium dodecylsulfate (SDS) is a good anodic inhibitor very close to the rest potential. The inhibition efficiency copper corrosion increases with an increase in concentration [84].

Benzotriazole (BTA) is a well-known organic inhibitor in acidic medium. It contains a nitrogen-based polar group. These nitrogen atoms act as electron donors andenhance chemisorption on the surface of the metal [85-87] the vacant ‘d’ orbitals in copper atom

form coordinate bonds with electron donating atoms such as nitrogen. Additionally, there is also interaction with rings containing conjugation, and these result in corrosion inhibition [88]. BTA shows two polymeric structures, depending on the nature of the copper oxide present. Cuprous oxides yield Cu(I) BTA, which consists of linear polymeric chains. Cuprous oxide yields Cu(II) BTA, which has a network structure. BTA is the only inhibitor that provides effective protection to copper archeological artifacts during preservation process [89].Tolytriazole is superior to benzotriazole and it is used as anti-corrosive additive in cooling and hydraulic fluids, antifreeze formulation, aircraft deicer and anti-icer fluid (ADAF) and dishwasher detergents for silver protection[90-91].

ROLE OF pH

The solution pH is a very important factor in the electroless deposition. The deposition rate, surfaces morphology, the roughness and the crystallinity depend on pH [92].Oxidation of the reducing agents employed in electroless copper plating invariably involves the formation of either hydrogen (H') or hydroxyl (OH^-) ions. Consequently, the pH of the plating solution changes during plating and thus affects the rate of deposition and the properties of the deposit. When *p*H increases, the free metal ion concentration of the solution also increases. Therefore, buffers are added to stabilize the pH of the solution. These include carboxylic acids in acid media (which also act as cornplexants) and organic amines in alkaline solutions.KOH is the better pH adjuster than NaOH, because it can alter film properties and increase the solubility of byproducts formed.

EMERGING APPLICATIONS IN ELECTROLESS COPPER PLATING

During the late 70’s and 80’s, the future of electroless plating seemed gloomy, but with increasing demand in electronics, space, defence and other engineering industries, the commercial applications of deposition processes have increased many-folds.

(i) Recently, electroless deposition has been used in the metallization of carbon nanotubes [93-94] and the formation of metal nanoparticles [95]and nanowires [96-97].Yagi et.al [98] produced copper nano particle electrochemically using hydrazine aqueous solution and dispersed CuO. Hydrazine is the reducing agent that reduces the oxide to metal. The rate of Cu nanoparticles formation was examined using an in situ micro balance (QCM).

(ii) Electroless deposition of metals on polymers and plastics has also been an emerging application of the process [99].Polymers can be used as substrates in both electrolytic and electroless metal deposition. Copper coated polyimide (PI) films are used as flexible copper clad laminates (FCCL) in electronic industry. Electroless copper coated plastics such as acrylonitrile butadiene styrene (ABS), polyethylene terephthalate (PET) fabricates [100] polypropene, teflon, are widely used in PCB's, automobile parts and EMI applications [101-103].

(iii) Production of lightweight metal composites is an interesting application of the electroless copper plating technique. An out-of-the-box idea of copper coating to produce lightweight composites has been reported by [104] who has coated pollen, the lightweight powder found on the stamen of flowers with copper using electroless plating. They have used palladium as a catalyst. The pollen core/copper shell type nanocomposite spheres have been proposed as a novel lightweight material conductivity comparable to metallic copper [105].

(iv) Electroless copper has been proposed as an interconnect metal for submicron integrated circuit technology. A simple reason is that copper is a better conductor than aluminium. Copper can thus reduce interconnect RC delay time. Electroless plating can produce high quality deposits with good via trench filling capability. The fabrication of high performance multilayer boards via, plated through hole interconnection is based on electroless copper plating.

(v) Electroless copper plating technique has been successfully used to coat mica [106], graphite [107-108], iron [109] and fly ash ceneosphere particles[110] to impart electrical conductivity to those non conducting oxide ceramic particle. Copper coated ceramics can be employed in microcircuits used in radar and in communication equipment used in railways and electricity boards, post and telegraph offices and in space vehicles [111].

(vi) The feasibility of using electroless copper deposition on integrated circuit (IC)[112] interconnections and application for IC fabrication has been demonstrated by Ting and co-workers [113-114]. The work has been done on non-catalytic and catalytic surfaces. The need for finer geometry, denser circuitry, higher quality and better reliability of end products has spurred interest in the development of newer, more

efficient manufacturing processes for PCB's [115]. Solder joint reliability and the corrosion resistance of PCB's surface finish are particularly of great interest [116-117] in addition to cost benefits and environment aspects.

(vii)Electroless copper coating methods are used in micro technology. Electroless copper and its alloys are being increasingly used as materials for interconnects and packing applications for ultra-large-scale integration (ULSI) [118-120].Electroless deposition of copper is one of the major process steps involved in electronic packaging for the computer industry [121]. It is also used for various metallization processes such as carbon nanotubes or hollow metal spheres. Electroless copper has proved to be effective in repairing nanoscale defects in the seed layer [122].

CONCLUSION

The literature study of electroless copper plating led to the following conclusions:
EDTA has excellent chelating properties over a wide *p*H range but is not bio-degradable and produces serious pollution problems. Triethanolamine (TEA) has plating rate about 20 times higher than EDTA.In recent days eco-friendly, bio degradable polyhydroxylic compounds are gaining importance as chelating agents in alkaline medium as potential replacements to EDTA. Glyoxylic acid results in better plating rates and bath stability than formaldehyde and hypophosphite. The rate of the Cannizzaro reaction with glyoxylate ions could be reduced by KOH as buffer in plating bath. Compounds having planar and other structures with lone pairs of electrons such as sulphur and nitrogen containing organic compounds have been proposed to serve as stabilizers The additives were found to modify the crystal structure with the production of small grain size, dense, tightly adherent and etching resistant copper deposit.

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