Studies on Plating Bath Requirements in Electroless Copper Deposition - A Review

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Abstract

This article is aimed at reviewing literature on the range of electroless plating bath requirements employed in electroless copper deposition. Owing to a range of superior properties, electroless copper is considered as an excellent choice in industrial applications. To overcome environmental issues associated with conventional copper electroless plating involving cyanide bath, EDTA bath, other toxic plating baths, and the eco-friendly progress are now being developed. Polyhydroxylic compounds are gaining attention as potential complexing agents which are eco-friendly. Similarly, biodegradable reducing agents have been proposed to be effective in electroless copper plating. The achievements of organic additives containing sulphur and nitrogen atoms with lone pair of electrons are also noticed. Influences of other bath parameters such as pH and buffer on surface morphology are summarized. Recent trends in the applications and advancements in electroless copper plating have been reviewed and discussed.

Key words: biodegradable, copper deposition, organic additives, polyhydroxylic compounds, surface morphology.

I. INTRODUCTION

Electroless plating is a method of noble metal deposition from its salt on a catalytically active surface by employing an appropriate reducing agent without necessarily passing electricity. Otherwise known as autocatalytic process or conversion coating of depositing a metal from its solution in the absence of applied external potential. The minimum requirements of this process are a metal salt and a fitting reducing agent. This process also makes use of additional requirements such as complexing agents, additives, optimum pH and optimum temperature. Parameters of concern for this process are attaining coatings with uniform thickness, deposition on irregular surfaces, high selectivity, outstanding step coverage and admirable filling capacity.

The history of electroless plating dates back to the serendipitous discovery of electroless nickel phosphorous alloy reported at the 34th Annual AES meeting by Abner Brenner and Grace Riddell [1] in 1946. This tremendous discovery has thus far opened great windows of opportunity in numerous industrial applications, and commercially essential for finishing steel, aluminium, plastics, glass, composites and numerous material surfaces.

Electroless plating on copper started in 1947, when Harold Narcus [2] established about "Practical Copper reduction on non-conductors". Yet, it was in the mid of 1950, that electroless copper plating gained commercial value. The products resulted tend to be very hard and less porous, thereby increased corrosion resistance. These properties facilitated electroless copper platings in oil fields and marine applications on parts like pumps and valves which are frequently subjected to corrosion. It may
be a better alternative for coating for complicated shapes as well. Pioneers like Cahill [3] and Wein [4] rooted for the commercial applications of electroless deposition.

Electroless plating is applied in the field of nanotechnology for the production of photo masks and micro devices with nanosized adjacent elements of different thickness made of various materials by single conventional optical photolithography. Electroless deposition is generally explained on the basis of ‘mixed potential theory’ which was proposed by Wagner and Traud [5] in 1938. This theory proposes that electroless deposition encompasses cathodic and anodic partial reactions occurring simultaneously on the substrate surface. However, there is a limitation to the application of mixed potential theory to electroless plating. Both the half reactions are not independent of each other studied by Donahue [6] in 1972, but measurements to clearly demonstrate was given later by Bindra et al. [7] by performing kinetic and mechanistic measurements in the catholyte and the anolyte, as well as in the complete electroless copper bath separately. Theoretical conditions pertaining to electroless plating can be established with the help of Pourbaix diagrams [8]. This shows the potential and pH range over which several oxides, ions and pure metals are stable thermodynamically. Sufficient quantity of studies has been reported related to the kinetics of electroless copper deposition ([9]-[13]). Majority of them have analyzed results with respect to classical kinetic theory and employ the following rate equation:

$$r = k[Cu^{2+}]^a[OH^-]^b[HCHO]^c[Ligand]^d$$

(1)

The rate determining step for the electroless copper bath is most frequently related with the anodic process, which is controlled kinetically. The assessment of catalytic activity of different metals and the oxidation of common reducing agents can be attained by studying electrochemical techniques. Studies on the polarization nature of a several reducing agents on a variety of solid electrodes were carried out by Ohno et al.[14] and determined that copper is most catalytically active for formaldehyde oxidation, when compared with other familiar reducing agents. The properties and grain structure of electroless copper deposits are dependent on the substrate upon which the deposition occurs. The grain structure associated with a conducting catalytic substrate differs markedly from that obtained on an activated or catalyzed non-conductor.

### Major types of copper baths and its properties

There are four major copper baths preferentially used in electroless copper plating processes.

1) Copper sulphate bath: The advantages of this bath are its good throwing power and low cost.
2) Copper cyanide bath: This bath results in high adhesion and very rapid plating.
3) Copper pyrophosphate bath: This bath produces ductile coatings and has high throwing power.
4) Copper fluoborate bath: This bath boasts of high plating speed.

### II. ROLE OF COMPLEXING AGENTS

Complexing agents greatly influence the reductive potential of cupric ions in the presence of a strong alkaline medium due to the formation constant of the complex, which affects the mixed potential, thereby has an effect on the copper deposition. Complexing agents enhance bath stability, improve deposit quality and plating rate. They also diminish the conversion of copper to copper hydroxide Cu(OH)$_2$ under alkaline environment. The complexing agents employed in the electroless copper plating will carry out the following functions.

1) Stabilization of sudden decrease in the pH of the electroless bath by their buffering action.
2) Prevention of the precipitation of copper salts.
3) Reduction in free copper ion concentration.

The correlation between the ligand concentration and plating rate was investigated by De Minjer and Brenner [15]. The addition of complexing agents in small concentration will result in an increase in plating rate. As the ligand concentration further increases, the adsorption on the surface also increases which leads to the poisoning of the catalyst and consequently
decreases the plating rate. Several theories have been proposed to explain the relationship between ligand concentration and maximum plating rate [16].

Conventionally, complexing agents used for electroless copper plating have been quite often categorized into one of the set of compounds such as alkanol amines, quadrol, EDTA, triethanolamine, tartarate salts, glycolic acid etc. Addition of complexing agents results in high metal ion concentration and an improved end product. Ethylene Diamine Tetraacetic Acid (EDTA) has long been viewed as a potential complexing agent that has excellent chelating property over a wide range of pH, weak adsorption on copper and maintains bath stability ([17]-[20]). EDTA has superior complexing ability than tartarate and can be operated at low temperature ([21],[22]). But EDTA has poor biodegradation, and raises environmental concern. Moreover, its effect in mobilizing heavy metals from solid phases poses a risk of ground water contamination and health hazards.

In 1960’s alkanolamines were extensively used to accomplish faster plating rate and “high build” deposits. Triethanolamine (TEA) enhanced Cu\(^{2+}\) reduction more than EDTA and also reduces formaldehyde oxidation. In dual chelating EDTA and TEA systems, TEA shrinks the grain size, but yields uniform grain size due to the addition of EDTA [23]. TEA is associated with increase in deposition rate and reduction in roughness of deposited film which would result in a promising improvement in mechanical and physical properties [24]. In comparison with EDTA, addition of TEA resulted in faster and maximum deposition rate ([25]-[27]). Effects of EDTA and TEA individually and EDTA - TEA dual systems on Pd activated epoxy resin were investigated. The EDTA bath has led to low deposition rate and high bath stability, whereas, TEA bath has resulted in weaker complex than EDTA and high deposition rate. In EDTA- TEA dual system, reasonable bath stability and deposition rate were observed [28]. Triisopropanolamine has been found to aid in high deposition rate along with bath instability and poor quality deposit[29]

Tartarate salts are found to be effective only at low temperature and would result in low plating rate ([30],[31]). On the other hand, it has the benefit of easy effluent treatment. But it is not suitable for systems, where faster plating is preferred. Peng et al. have studied the influence of tartarate bath and dual chelating tartarate and EDTA bath and reported that the deposition rate of tartarate bath was relatively faster than dual chelating tartarate and EDTA bath [32]. Iminodiacetate complexing agent has been reported to have a comparable deposition rate with that of EDTA, whereas, the scope of iminodiacetate for pH alteration is fairly broad, and yields a thicker copper deposit than EDTA bath [33].

Recently, Polyhydroxylic compounds have garnered interest as suitable alternative to traditional complexing agents in electroless plating since they are eco-friendly [34]. In alkaline environment, they form stable complexes with Cu\(^{2+}\), leading to low concentration of free Cu\(^{2+}\) that prevents the precipitation of Cu(OH)\(_2\) and do not form metal complexes in neutral pH found in waste water treatments ([35],[36]). In electroless copper plating, the plating rate decreases, as the number of OH groups increases in the polyhydroxylic alcohols [37]. Comparative investigation on the influence of Xylitol, D-mannitol and D-sorbitol on plating rate has been reported[38]. At low concentration of xylitol, Cu(OH)\(_2\) is precipitated, whereas at higher concentration, no precipitation occurs. D-mannitol and D-sorbitol, do not form Cu(OH)\(_2\) precipitate at both low and high concentration. Maximum plating has been observed at pH 13.4 for D-sorbitol and at pH 13.8 for D-mannitol. An investigation has been reported in the fact that in alkaline Cu(II), D-mannitol solutions mannitol behaves as a ligand in a manner somewhat analogous to xylitol[39]. For xylitol based MSA bath copper deposition begins at pH 12.5 reaches a maximum at 13.25, and is stable up to pH 13.5[40].

Investigators have thus far reported satisfactory results on employing glycerol as a complexing agent ([41],[42]). Another eco-friendly complexing agent that has been widely used nowadays is saccharose ([43],[44]). Saccharose bath yields maximum plating at pH 12.75, and then slows down at higher pH. The copper deposits obtained in the saccharose bath were sand-like in morphology. Furthermore, addition of 2,2-dipyridyl resulted in smooth and shiny deposits[45]. A comparative
investigation on isomers on tartaric acid, namely D- tartarate, L-tartarate and racemic mixture has reported that the maximum plating rate reaches about $2.0 \mu m h^{-1}$ at pH 12.5 for racemic mixture, $1.4 \mu m h^{-1}$ at pH 13.0 for L isomer and $0.9 \mu m h^{-1}$ at pH 12.5-13.0 for D isomer [46]. Additionally various complexing agents such as glyc erine, sucrose, erythritol, trisodium citrate, adonitol, lactitol, dulcitol, maltitol have the potential to be looked upon for recent investigations ([47]- [49]).

III. ROLE OF REDUCING AGENTS

A reducing agent is a primary requirement for electroless plating technique. It facilitates the reduction of metal ions and results in the formation of deposits on the auto catalytic surface. Several reducing agents such as formaldehyde, hypophosphate, glyoxylic acid, hydrazine, borohydride, dimethylamine borane have been thus far employed in numerous experimental conditions ([50]-[54]). Conventional electroless copper plating baths employed primarily formaldehyde as the reducing agent. A large number of experimental works on formaldehyde baths have been reported till date. On usage of formaldehyde, electroless copper plating can be expressed as two half cell reactions.

\begin{align}
2\text{HCHO} + 4\text{OH}^- \rightarrow 2\text{HCHO}^- + \text{H}_2 + 2\text{H}_2\text{O} + 2e^- & \quad (2) \\
\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} & \quad (3) \\
\text{Overall reaction} & \\
2\text{HCHO} + 4\text{OH}^- + \text{Cu}^{2+} \rightarrow 2\text{HCHO}^- + \text{H}_2 + \text{Cu} + \text{H}_2\text{O} & \quad (4)
\end{align}

Utilization of formaldehyde in commercial electroless plating is attributed to cost effectiveness, good quality deposits and ease of control of formaldehyde systems. In formaldehyde bath systems $E^0$ depends on pH of the bath. Small additions of ammonia in formaldehyde baths at 20³-30³ C resulted in enhanced deposition rate by a factor of 2-4, has been observed. Consequently, on using formaldehyde, pH should be maintained above 12[55], which poses a problem of alkaline corrosion of the electrolyte. Formaldehyde has also lost its charm as an effective reducing agent owing to environmental concerns raised by environmentalists. Additionally, it poses health threats like, respiratory irritation, occupational asthma and is carcinogenic as well.

Administration of sodium hypophosphate as a reducing agent replacing formaldehyde can be attributed back to 1960s. It gathered attention as a good reducing agent due to its low cost, effectiveness at low pH and relative safety. Brookshire was a pioneer in using hypophosphate bath [56]. In 1980, Kukans et al.[57] received a patent for electroless copper plating using hypophosphate. Xueping et al.[58] obtained brown copper deposits with high electrical resistivity in hypophosphate bath.

Hypophosphate bath with little addition of Co ion, yielded pink deposits with good conductivity and surface adhesion [59]. Considerable amount of hypophosphate bath literature have been reported at high temperature with improved plating rate and deposits with enhanced physical properties ([60],[61]). Despite possessing commendable advantages, hypophosphate holds some limitations that its oxidation is not catalyzed by copper, leading to meagre or no plating of copper. This can however can be overcome by addition of Nickel catalyst.

Limited researches have been carried out on using hydrazine as reducing agent, owing to unfavourable bath stability and film deposition. By products obtained from hydrazine baths such as H₂O and N₂ are eco-friendly. On using phenyl hydrazine, it was difficult to obtain a coherent copper film on plate glass surfaces, due to the formation of tarry by-products, which appear predictably to result when such a reducing agent is used. French E.A studied extensively the usage of phenyl hydrazine and documented the difficulties like requirement of high temperature and skin problems due to irritating flames involved in it [62].
Hydrazine sulphate, despite possessing advantages of greater solubility in water, low cost and less poisonous, success is dependent on varied temperature. Nobari et al[63] have investigated Pd free deposition of copper on glass with hydrazine and concluded that excess amount of hydrazine resulted in poor coating. They reported that the deposition growth rate increases with increase in the ratio of \([\text{N}_2\text{H}_4] / [\text{Cu}^{2+}]\) upto 2 and then decreases when the molar ratio is more than 2.

Glyoxylic acid has also been employed as an alternative reducing agent in various literature. The prospect of employing glyoxylic acid was first proposed by Darken [64]. In 1994 Honma et al[65]. confirmed that absence of vapour pressure and better reducing capacity makes glyoxylic acid a fitting alternative to formaldehyde. It also nullifies environmental and health problems. It results in increased plating rate and higher bath stability than formaldehyde baths. Doubling the concentration of glyoxylic acid at constant pH improves the deposition rate by a factor of < 50% [66]. When adding KOH in glyoxylic acid bath, consumption rate of glyoxylic acid is reduced and mechanical properties of coating are enhanced [67]. Copper coating on several surfaces using glyoxylic acid has been reported as well ([68],[69]).

Dimethylamine Borane has also garnered attention as a potential reducing agent in electroless copper plating [70]. It has good solubility, better workability, no toxic fumes and can be operated at varying temperature. A high quality copper deposit with amine borane at pH 9 has been reported. Increased plating rate and high adhesion rate have also been reported in DMAB plating baths ([71],[72]).

In addition to the above discussed reducing agents, several other reducing agents such as phosphinate, borohydride and ascorbic acid [73] have also been investigated by research community, yet the applications are minimal, because bath stability and coated layer properties are not favourable.

IV. ROLE OF METHANESULPHONIC ACID

During the early 1980’s methanesulphonic acid (MSA) became a potential electrolyte for numerous metal coating applications. Methanesulphonic acid is a transparent pale-yellow liquid, soluble in water, partly soluble in organic solvents like benzene and its derivatives, but highly insoluble in paraffins. They are the simplest of the alkylated sulphonic acids and has the chemical formula of \(\text{CH}_3\text{SO}_3\text{H}\). MSA is a strong electrolyte and its conductivity in water is similar to other strong acids such as sulphuric or hydrochloric acid and higher than that of other organic acids.

The following characteristics make MSA as a green solvent

1) Odour and toxic fumes free thereby making it safer.
2) Readily biodegradable, forming sulphate and \(\text{CO}_2\).
3) Recyclable due to its excellent solubility in water.
4) High strength makes it a good catalyst of many organic transformations.

The Bronsted acid, methanesulphonic acid (MSA) is a strong acid, non oxidising and stable at high temperatures upto 180°C. It has replaced the conventionally used fluoroboric acid in plating applications. Moreover MSA’s superiority over other bath liquids arises from its excellent metal salt solubility, brilliant conductivity, ease of effluent treatment, stability, well defined chemistry and bio-degradability ([74],[75]) and it can be operated at room temperature. MSA is considered as an intermediate between sulphuric acid and methyl sulphonyl methane. It helps in maintaining the necessary \(p\text{H}\) for effective progress of the reaction.
**V. ROLE OF OTHER ADDITIVES**

Electroless plating baths are generally short lived and are probably prone to decomposition. To overcome these difficulties, certain compounds called additives or stabilizers are added there modifying physical and mechanical properties of the coating ([76], [77]). They may be organic or inorganic in nature. Additives could perform as inhibitors, levellers, brighteners or wetting agents in the electroless plating process. They have an effect on kinetics of plating mechanism, purity, structure and morphology of the surface coating ([78]-[81]).

1) Inhibitors such as polyethers and polyoxyethers enhance the throwing power in complicated parts and form monolayer film on the substrate surface. They also prevent the diffusion of Cu^{2+} onto surface by forming a barrier and reduce plating rate.

2) Levellers like amines, organic nitrogen compounds and amide surfactants lower the plating rate by getting strongly adsorbed on the surface at high current density regions and improve thickness and uniformity of plating.

3) Brighteners speed up plating rate and control grain structure and deposit properties. They increase the charge transfer at the electrodes and manage deposit hardness and brightness by getting attached to copper ions. Example: Compounds containing sulphur.

4) Compounds such as sulphonated alcohols and sulphonates of fatty acids aid in the wetting of electrolyte at the electrode by decreasing the surface tension of the bath solution. The functions of additives are influenced by factors such as temperature, pH, concentration of reducing agents and presence of impurities.

5) The most commonly used additives in the electroless deposition baths are polyethylene glycol (PEG), Sodium Dodecyl sulphate (SDS), amino acids, azole compounds, thio-urea, bipyridyls and much more. They alter the size, shape, brightness and orientation of the surface deposits. Some heavy metal ions (lead, tin, bismuth, thallous ion in nickel bath) can also be used as stabilizers. The concentration of many stabilizers is in the range of 0.1 to 200 ppm. The effects of inorganic additives as stabilizer have also been investigated [82].

Organic compounds containing heteroatoms such as sulphur and nitrogen with lone pairs of electrons and compounds having planar structures have been anticipated to be engaged as stabilizers [83]. For instance, compounds such as pyridine, cytosine, guanidine, hydrochloride, 2-mercaptobenzothiazole (2MBT), KCN, potassium ethyl xanthogenate, benzotriazole (BTA), dithiocarbamate ([84]-[85]) and 2,2’-dipyridyl ([86]-[88]) have been studied as well.

Cyanide ions behave as exhalant and are known to improve the ductility of electroless copper deposits and increase the bath stability at elevated temperatures. They adsorb strongly on copper surface and facilitate the desorption of hydrogen gas from the deposit surface [89]. Nakahara compared the ductility ranges of the deposits obtained with various metal cyanide additives. The highest ductility of ~12% was obtained in the presence of K_4[Fe(CN)₆] along with polyethylene glycol[90]. Cyanide and Gafac have been utilized as brightening and levelling agents in copper plating baths and have a commendable effect on the crystal growth leading to superior surface properties [91]. The effect of potassium ferrocyanide K_4[Fe(CN)₆] in the presence of PEG, MBT and pyridine have been studied. At higher concentration of K_4[Fe(CN)₆], inhibition effect decreases and levelling effect is achieved, when PEG and K_4[Fe(CN)₆] coexist[92].

Adenine and guanine have been identified to perform as accelerators due to the presence of N atom, π electron density, and also curb the oxidation and passivation of metallic copper in alkaline environment in electroless copper deposition. Sulphur compounds have also been used in conjugation with nitrogen compounds like nitrile [93]. Paunovic reported that adenine and guanine act as accelerators whereas coumarin and saccharin have almost no effect on electroless copper plating [94]. The addition of guanine to the bath appreciably reduces copper diffusion through the layer, while the addition of adenine stops copper diffusion altogether. These complexes reduce the number of Cu^{2+}-carboxylate complexes formed and consequently decrease the of Copper plating rate [95].
The sulphur compounds such as thiourea, generally act as stabilizers ([96]-[98]). A decrease in copper plating has been observed together with an appreciable hole filling capacity on adding thiourea [99]. At high thiourea concentration, reduced plating rate with uniform thin deposits and increased bath stability have been reported [100]. Thiourea derivatives have been found to act as stabilizers and hinder the copper plating rate owing to their effective adsorption on metal surface [101]. An exceptional case of thiourea enhancing the deposition rate has also been reported.

Glycine and cytosine inhibit corrosion. Higher glycine concentration lower the free formaldehyde concentration and subsequently decreases the plating rate and increases ductility and tensile strength of the copper deposits.

Benzotriazole (BTA) can be documented an organic inhibitor in acidic medium. Polar nitrogen atoms present serve as electron donors and boost chemisorptions on the metal surface ([102],[103]). The unoccupied ‘d’ orbitals in copper atom form coordinate bonds with electron donating nitrogen and there is an interaction with rings containing conjugation, imparting corrosion inhibition [104]. Benzotriazole addition produced the copper deposits with finer and more compact structure than imidazole and plain baths. In addition, deposits were smooth and shiny.[105]. Balaramesh et al have done a comparative study on the stabilizing influence of aminotriazole (ATA), benzotriazole (BTA), and tolytriazole (TTA) in the electroless copper deposition. All three triazole stabilizers have been proved to prevent the bath decomposition and extend its lifetime, whereas ATA has an inhibiting effect and BTA and TTA have exhibited an accelerating effect on the plating [106].

Several triblock copolymers have also been accounted to be contributing as inhibitors in electroless copper plating ([107]-[110]). Polyethylene glycol (PEG) is also looked upon as an inhibitor in formaldehyde bath and a surfactant in glyoxylic acid bath ([111],[112]). Investigation by Osborn et al. have concluded that, PEG has an inhibiting action at high temperature, leading to controlled plating and good quality copper deposits without excessive porosity [113].

Ammonia acts as an effective accelerating agent in autocatalytic reduction of Cu(II) by formaldehyde in EDTA solutions (At 20°– 30°C, rate of copper plating increases 2–4 times) and enhances real surface area [114]. L.S. Li et.al reported that when sodium dodecyl sulphate(SDS) were added to the bath, the deposition rate reached 3.45 μmh⁻¹, and the resulted copper deposits were smooth and uniform [115]. It has been found that, the plating rate decreases with the administration of 2,2- bipyridyl, to electroless copper bath, inhibits the catalytic oxidation of hypophosphite and resulted in semi bright highly uniform deposits[116]. Numerous additives such as pyridine, 1,10 phenanthroline, and sodium thiosulphate identified to be employed in electroless copper deposition have been reported in literatures([117]-[119]).

VI. ROLE OF pH AND BUFFER

Just like every other bath requirements for effective electroless copper deposition, optimum pH and maintenance of pH is also an important criterion to be taken into consideration for successful outcome. The primary and secondary pH effects have a direct and indirect influence on the phenomenon related with the structure and composition of metal solution interface [120]. Due to the oxidation of reducing agents, H⁺ or OH⁻ ions are liberated, subsequently altering the pH of the plating bath, which has a great deal of effect on the plating rate and properties and quality of deposits.

In hypophosphite bath, plating rate increases remarkably from 2 to 6.5μmh⁻¹ when the solution pH increases from 5 to 9 [121]. Negative impacts are also possible on alteration of pH. Hence, it gains great significance in maintaining pH of electroless plating baths, by addition of appropriate buffer for better results. Salts of hydroxy acids and dicarboxylic acids can serve as buffers in acidic electroless plating bath. Organic amines, KOH and NaOH are employed as buffers in alkaline medium. In certain cases complexing agent performs the action of buffer as well. Borates and phosphates were also used as buffers, which influenced the rate of electroless deposition [122].
VII. NOVEL APPLICATIONS OF ELECTROLESS COPPER PLATING

Electroless plating of metals and alloys, serves various useful functions in electronic devices for corrosion protection, diffusion barriers, conductive circuit elements, via-hole filling for semiconductor integrated circuits, through-hole connections for printed wiring boards and flexible circuits ([123],[124]). Plating is used to fabricate passive devices on dielectric surfaces such as resistors, capacitors, inductors and to improve conductivity of metallised circuits. Diffusion of metals can let oxidation that alters the sought-after characteristics of the device. Even a small amount of diffusion into the plating can alter conductivity.

Electroless processes are simple, low cost and easy to execute. Printed wiring boards or printed circuits boards (PCB) also called the plated through-hole process use electroless copper for connecting one side to another. Additive circuits are also made using electroless copper and can be deposited on non-conducting substances. Electroless plating of solid metals from a solution has been widely used in the printed circuit board industry for production of wiring layers and inter-layer (via) connections and more recently for the production of metal interconnect films in the integrated circuit substrate (IC substrate) industry. Electroless copper has been anticipated as an interconnect metal for submicron Integrated circuit technology.

Electroless copper plating procedure has been successfully employed to coat numerous substrate surfaces such as mica, iron, graphite and fly ash ([125]-[128]) and also have been used in the metallization of ceramics in ultrasonic field [129]. Copper coated ceramics employed in microcircuits are used in radar and communication equipments utilized in railways electricity boards, post and telegraph offices and in space ships [130].

Electroless copper plating is also engaged in the metallization of carbon nanotubes, and has been proved to be effective in repairing nanoscale defects in the seed layer ([131],[132]). Electroless copper plating have been applied to non conventional surfaces like pollen, the light weight powder found on the stamen of flowers which has a potential to behave as a novel lightweight material with better conductivity comparable to metallic copper and Fraxinus mandshurica veneer wood for synthesizing EMI shielding composites ([133]-[135]).

Electroless copper coated polymer such as acrylonitrile butadiene styrene (ABS), polyethylene terephthalate (PET) fabricates, polypropylene and teflon, are extensively employed in PCB’s, automobile parts and EMI applications ([136]-[139]). Recently, a study has been reported regarding the production of low weight components for antenna applications and radio-electronic devices with enormous variety of shape [140].

VIII. CHALLENGES FOR NANO METAL DEPOSITION

Electroless plating, in spite of possessing of many advantages, it has its own share of challenges that needs to be taken care of to arrive at successful deposition. The complexing agent, reducing agent, additives and the buffer must be added in accurate concentrations and optimized. The temperature and the purity of the bath components are also important. The bath instability will lead to slow deposition rate, dull deposits and improper coverage and presence of impurities may gravely affect the plating process and hence impurities, if present must be properly removed.

The substrate must be subjected to appropriate pre-treatment and cleansing, since improper substrate surface preparation will result in uneven coatings, poor adhesion, dull and porous deposits. Proper agitation of the bath must be done to avoid rough deposits and to reduce plating cost. Eventually, electroless process should be carried out with highest care and purity to avoid improper adhesion and coverage and for desired better results.
IX. Conclusion

The following conclusions have been made on the basis of this review of literatures. Even though, formaldehyde and EDTA have been found to enhance the electroless copper deposition quality, they tend to pose environmental and health problems. Hydrazine is eco-friendly, still does not contribute much to bath stability. Researchers now gained more attraction towards substituted amine boranes and glyoxylic acid for attaining improved bath stability and enhanced plating rate.

Employment of environmentally sustainable polyhydroxylic compounds as complexing agents have secured interest among research community. Heteroatomic organic additives possessing nitrogen and sulphur with lone pair of electrons are considered to be better options as stabilizers in electroless copper deposition.

The magnitude of application of electroless copper plating in sectors like, PCBs, electronics, telecommunications, Integrated circuits, Information technology, satellites and nanotechnology has fired up the minds of so many researchers and more research in this field would definitely produce innovative inventions in the future.

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