

Studies on the Influence of Electroless Copper Deposition Process – A Review

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Abstract: *Electroless copper deposition involves several simultaneous reactions in an aqueous solution, which occur without the use of external electrical power. The electroless deposition of copper is based on the incorporation of a reducing agent into the electrolyte and is initiated by a catalyst on the insulating catalytic surface, metals and non-metals. Once the metal nucleus is initiated, the process formulates into an autocatalytic process where the copper metal itself serves as the site for oxidation of the reducing agent. In addition to the deposition of copper metal nuclei, the catalyst site serve as the adhesive link between the depositing copper metal and the insulating surface. Since the reaction is thermally unstable, the thermal stability of the bath solution is increased by the addition of the complexing agents and stabilizers to the copper metal ion. This present work involves the effect of complexing agents, stabilizers and reducing agents on the rate of deposition and the bath stability. Electroless copper deposition process is cost effective and environment friendly because it does not require any vacuum equipments, such as sputtering, evaporation and chemical vapour deposition, or power supplies and seed layers, such as in electroplating. Copper is the best metal of choice for interconnect in integrated circuits and electronic packages because it has low resistivity and high electro migration resistance. Emerging application of this technique provides a scope to plate electromagnetic interface shielding materials, polymeric nanoparticles and in the field of aerospace, biomedical and energy conversion etc. The main advantage of this copper electroless deposition process is that it can be plated in non conductive surfaces with metal coatings of uniform thickness all over the plated object.*

Keywords: *Electroless deposition, Stabilizers, Complexing agents, reducing agents, sputtering*

I. INTRODUCTION

Electroless deposition 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 any applied potential. Electroless deposition is categorized into three types, viz., autocatalytic process, galvanic displacement, and substrate – catalytic process. The first process, where, as the name suggests, the metal itself acts as the catalyst to deposit more metal on it, is fundamentally different from the later two. In autocatalytic deposition, the thickness of the deposit continues to increase as long as there is metal ion in the solution, because the deposited metal itself possesses catalytic activity. In the other two processes, the deposition stops when the substrate is covered completely with the deposited metal. These two processes metal ions receive electrons from the reducing agent, resulting in metal deposition (Schlesinger M., et al., 2000; Schlesinger M., et al., 2010;[1-2].

Electroless plating can be carried out on insulator, metallic or non metallic, non conducting surface (Bhatgadde .L.G., et al.,1977; Ling. G.P., et al., 2005[3-4] including polymers ceramics, glasses and semiconductors. Electroless plating article possesses good mechanical, chemical and magnetic properties.

Electroless plating results in coating with improved corrosion resistance, decorative appeal, increased solder ability, enhanced strength, reduced friction, altered conductivity and paint adhesion. Electroless deposition in the field of nanotechnology allows production of photo masks and micro devices with nano sized adjacent elements of different thickness made of various materials by single conventional optical photolithography (Hirsch T.J., et al., 1990; Zabetakis D., et al., 2009)[5-6]. 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.

Copper is the present and future interconnect material in high end micro processors and memory devices because of its lower electrical resistivity and higher electro migration resistance than other metals. Electroless copper coatings provide protection for common metal surface exposed to corrosion and wear.

The corrosion protection is due to the low porosity of the coatings and the excellent resistance of copper to many liquids and most atmospheric conditions. Electroless copper prevents contamination and decolourisation of plasticizers, solvents, oils, glycols, monomers and gases by metals such as iron, nickel and aluminium.

This possess uniform thickness, high hardness, excellent wear and abrasion resistance, absorptivity, good adhesion and provides excellent base for coatings (Paunovic .M., et al., 1985; Shipley C.R., 1984)[7-8]. 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 (Kuhn H.H., 1993; Wang Xiao-li., 2005) etc. [9-10]. The first scientific description of Electroless deposition process may be attributed to German chemist Justus Von Liebig in 1835. He reported the Electroless plating of silver from silver salts on glass surface using aldehyde as reducing agent. Later in 1844, Wurtz observed Electroless Ni coating using hypo phosphite reducing agent. In 1900, Weiskopf D.F, and on 1907, Chattway F.D, plated copper on glass using formaldehyde as reducing agent[11-13].

Then controlled Electroless plating process was discovered by Brenner and Riddell in 1946[14]. In 1947, Narcus reported an optimum plating condition for Electroless plating[15].

Electroless copper deposit was first reported by Narcus[16] and the first commercial application was reported by Cahill[17] and Zblisky et al.[18]. In 1980, a large no. of composite coatings with varying engineering properties were produced. Cobley et al. and Larson et.al. reviewed on electroless Copper plating process with various parameters influencing the rate of deposition. Zhu, Schneider and their co-researchers investigated the Electroless Copper plating process using sulphur compounds as additives and found that the compounds enhanced plating rate [19-24].

A decorative copper plating process was developed by Yuan and his team members. Modified formulations have been recently developed that result in higher plating rate with extremely stable conditions under a wide range of operating conditions.

II. INFLUENCE OF COMPLEXING AGENTS

The theoretical basis of the Electroless copper deposition process has been studied by Pearlstien in Lowenheim's book [25-28] and has recently been reviewed by Mandich and Krulik[29] Deckert[30-32] Complexing agent prevents the precipitation of metal hydroxide by alkalis from electroless bath by depressing the free metal ion below the solubility product of metal hydroxide. Generally complexing agents are added to improve the free ion concentration, deposition quality and to increase the stability of the bath.

The chelating agents being electron donors also have considerable affinity for H^+ ion as well as for metal ions.

There are many complexing agents that were reported such as EDTA, TEA, Tartrate, trisodium citrate, Quadrol, Acetates, succinates, Aminoacetates, Malonates, Lactates, Glycolates and polyhydroxylic compounds[33-35]. Rochell salt (K-Na Tartarate) was used in the earliest baths as a complexing agent and continues to be used for low plating rates and low temperature applications and waste treatment options.

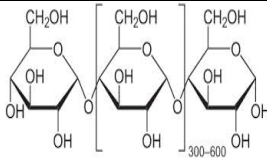
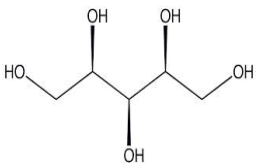
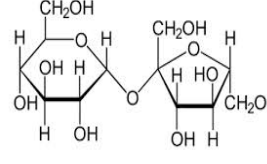
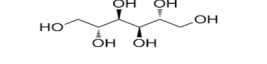
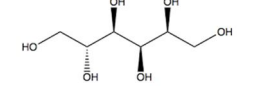
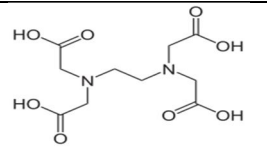
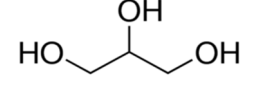
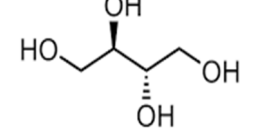
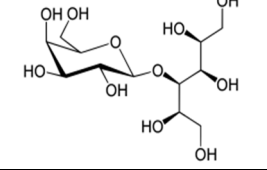
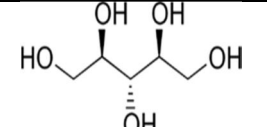
However it is not applicable in faster plating systems. In 1960s, Alkanolamines were used in wide range with the advent of fast plating system to achieve "high build" in electroless copper solutions. In 1970s EDTA salts were widely used for complexing agent in electroless copper solution.

For higher plating rates applied at higher temperatures, the most commonly used complexing agents are Ethylene diamine tetra acetic acid.

But EDTA is not biodegradable and forms complexes with heavy metals and increases the total nitrogen content of waste water and produces serious pollution problems in waste water. The SEM analysis of copper deposition with TEA as chelant showed shrinkage in the grain while grain size was more uniform with EDTA.

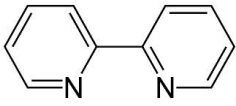
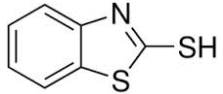
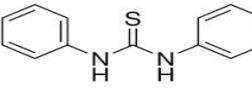
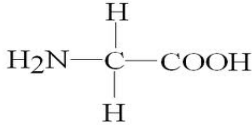
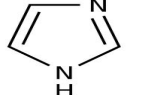
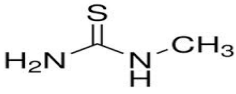
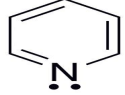
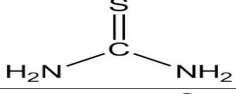
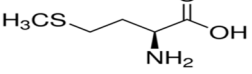
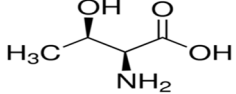
The polyhydroxylic compounds are more environmental friendly in nature and produces better result than other complexing agents because they are biogradable polyols which were reported in the late 20th century to form chelates with $Cu(II)$ ions in alkaline medium are potential replacements to EDTA.

Many natural polyhydroxylic compounds like glycerol, xylitol, saccharose, alditol, erythritol, adonitol, D-manitol, D-Sorbitol, maltitol, lacticol, dulcitol have been proposed as environmentally friendly chelating agents for alkaline electroless plating[36-38].

S.No.	Chemicals name/short form	Chemicals formula	Chemicals structure	Mole- cular weight (g/mol)	Chemical s make
1.	Starch	$(C_{12}H_{22}O_{11})_n$		342.3	Fisher
2.	Xylitol	$C_5H_{12}O_5$		152.15	Qualigen s
3.	Saccharose	$C_{12}H_{22}O_{11}$		342.29	Fisher
4.	D- Manitol	$C_6H_{14}O_6$		182.17	Merck
5.	D-Sorbitol	$C_6H_{14}O_6$		182.17	Merck
6.	Ethylene diaminetetra acetic acid	$C_{10}H_{16}N_2O_8$		292.24	Merck
7.	Glycerol	$C_3H_8O_3$		92.09	Millipore
8.	Erythritol	$C_4H_9NO_3$		122.12	Merck
9.	Lacticol	$C_{12}H_{24}O_{11}$		344.31	Merck
10.	Adonitol	$C_5H_{12}O_5$		152.15	Merck Millipore

III. INFLUENCE OF ADDITIVES / STABILISERS

Addition of few ppm of Stabilizers increases the stability of the bath, which reduces the deposition rate but increase the brightness of the coatings [39 – 45]. Additives that stabilize the bath against the formation of undesired cuprous oxide particles are referred to as stabilizers. This undesirable phenomenon can be controlled by bubbling air or oxygen through the bath as reported by Innes et al., [46] and Coombs [47]. Bieliaski and Kaminski (1987) have reviewed the use of inorganic additives as stabilisers. Over 200 papers and patterns have been published on the effects of large number of stabilisers on the plating solutions. 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 stabilisers [48]. Thiourea, N-Methylthiourea, Ethylenethiourea, N,N'-Diphenylthiourea, Allylthiourea, N-Penylthiourea, Diethylthiourea, pyridine, cytosine, guanidine hydrochloride, 2-mercapto benzo thiozole (2MBT), KCN, potassium ethyl Xanthogenate, poly ethylene glycol (PEG), dithio carbamate [49 - 53] and 2,2' dipyridyl etc. are some of the important compounds which are used as stabilisers. Tris-(hydroxyl methyl) amino methane increases the stability and deposition rate of EDTA based copper bath. It has been found that Selenium compounds behave much as sulphur compounds with the advantage that they are more stable at high pH and do not darken the plate. Examples are benzyl selenium acetic acid, Seleno cyanates and Seleno cyano acetic acids. Because of high cost and high toxicity, it is doubtful these compounds will find much use.

S.No.	Chemicals name/short form	Chemicals formula	Chemicals structure	Mole- cular weight (g/mol)	Chemicals make
1.	2,2'-dipyridyl	C ₁₀ H ₈ N ₂		156.18	Nice chemicals
2.	2-Mercapto-benzothiazole	C ₇ H ₅ NS ₂		167.25	Fisher
3.	Diphenyl-thiourea	C ₁₃ H ₁₂ N ₂ S		228.31	Merck-schuchardt
4.	Glycine	C ₂ H ₅ NO ₂		75.066	Merck
5.	Imidazole	C ₃ H ₄ N ₂		68.08	Qualigens
6.	N-methyl-thiourea	C ₂ H ₆ N ₂ S		90.15	Fluka AG
7.	Pyridine	C ₅ H ₅ N		79.1	S.d fine chem. limited
8.	Thiourea	CH ₂ N ₂ S		76.12	Merck
9.	l-Methionine	C ₅ H ₁₁ NO ₂ S		149.208	Merck
10.	l-Threonine	C ₄ H ₉ NO ₃		119.12	Merck

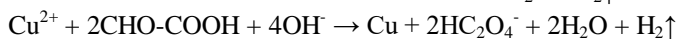
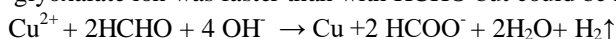
IV. INFLUENCE OF REDUCING AGENTS:

Wein [54] has published a comprehensive non critical review of reducing agents used in electroless copper solutions. Saubestre [55-57] on the other hand has published a critical review of the most promising reducing agents. The most important characteristic that the reducing agent is capable of is completely reducing divalent copper to metallic copper and not into the intermediate cuprous oxide.

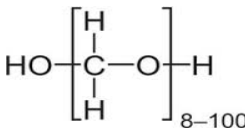
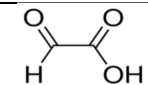
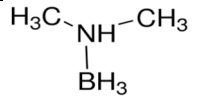


The important reducing agents in the literature are as follows:

Tartrates are used as reducing agents for silver and gold. The primary use of tartrate is to complex the copper ions preventing $\text{Cu}(\text{OH})_2$ precipitation in alkaline solution. **Traditional** electroless deposition uses formaldehyde as reducing agent. This has two main drawbacks: first formaldehyde is mainly efficient for pH values above 11, this high pH is incompatible with most forms of photoresist [58-59]. In addition this compound is considered as hazardous to health since their effectiveness increases with increasing pH. Hypo phosphate is an effective reducing agent in both acid and alkaline solutions. Brookshire [60] reported an electroless bath in which sodium hypo phosphite was used as a reducing agent. Glyoxylic acid is the best of all the replacement of HCHO because of its similar nature and properties which unlike formaldehyde, the glyoxalate ion in solution has no vapour pressure and the problem of HCHO contamination of atmosphere [61] Darken.J.Trans. Inst.Metal finish, 69 (2) stated that Plating rates and bath stability were superior to that of HCHO bath under standard conditions. The rate of Cannizzaro reaction with the glyoxalate ion was faster than with HCHO but could be reduced by 10% to 40% using KOH instead of NaOH.



Bamberger and Schweitzer [62] Eyber [63] French or others employed Hydrazine and its derivatives as reducing agents. But the optimum condition for the methods were ascertained by French [64-65]. A number of workers have investigated the electroless plating of copper using Dimethyl amine borane (DMAB) as the reducing agent. It does not produce toxic fumes and it can be run at a lower pH. Other reducing agents such as phosphanate, amino borane and phenyl hydrazine [66] but their applications are limited because bath stability and deposited film properties are not optimal [67-68].

S.No.	Chemicals name/short form	Chemicals formula	Chemicals structure	Mole- cular weight (g/mol)	Chemicals make
1	Para-formaldehyde	$\text{OH}(\text{CH}_2\text{O})_n\text{H}$ (n=8-100)		30.03 (As monomer)	Fisher
2	Glyoxylic acid	$\text{C}_2\text{H}_2\text{O}_3$		74.04	Merck
3	Dimethy amine Borane	$\text{C}_2\text{H}_2\text{BN}$		55.895	Merck

V. INFLUENCE OF pH

Maintenance of desired pH is very important in electroless deposition. The rate of deposition, morphology of surface, the roughness and crystallinity depends on pH [69] When pH increases, the free metal ion concentration of solution also increases. During the electroless deposition, there is a rapid change in pH. To overcome this, buffers are added to maintain the pH within the optimum range. NaOH, KOH and NH_4OH are general pH adjustors in electroless plating. Electroless copper deposition is affected by the pH in two distinct ways. OH^- ions are reactants in the overall reaction and the partial anodic reaction and thus influence these reactions in a direct way (primary pH effects). Second, pH affects various phenomena associated with the structure and composition of the metal – solution interphase. Those phenomenon includes 1) Adsorption, 2) The structure of the double layer, (3) The structure of the copper species in the solution, and 4) The ionic strength of the solution. All these phenomena modulate the rate of electroless copper depositon in an indirect way (secondary pH effects).

VI. SUMMARY AND CONCLUSION

Electroless copper deposition has attracted researchers in the recent years due to significant developments in electronic, energy devices, automotive, aero space and biomedical industries. If properly carried out, this is quite simple process produces on complex shapes very uniform and continuous coatings, which are difficult to obtain with other competitive technologies. Electroless deposition is a very important area of the modern technology, needs further developmental studies to ensure the successful operation of the process and desirable properties of the finally obtained material. Significant further work is definitely required to learn more about the kinetics and mechanisms of the reactions involved in these sophisticated processes.

REFERENCES

- [1] Schlesinger M., and Paunovic M., (2000), 'Modern electroplating'. 4th edition, New York, John Wiley. Vol. 14, pp. 868.
- [2] Schlesinger M., (Editor), and Paunovic M., (Editor), (2010), 'Modern Electroplating,' 5th Edition, New York, John Wiley, pp. 736.
- [3] Bhatgadde L.G., and Mahapatra S., (1977), 'Improved technique of electroless copper coating of alumina substrate.' Metal Finishing, Vol. 75, pp. 28-31
- [4] Ling G.P and Li Y., (2005), 'Influencing factors on the uniformity of copper coated nano-Al₂O₃ powders prepared by electroless plating.' Materials Letters., Vol. 59, pp. 1610-1613.
- [5] Hirsch T.J., Miracky R.F., and Lin C., (1990), 'Selective-area electroless copper plating on polyimide employing laser, patterning of a catalytic film', Appl. Phys. Lett., Vol. 57, pp. 1357-1359.
- [6] Zabetakis D., and Dressick W.J., (2009), 'Selective electroless metallization of patterned polymeric films for lithography applications', ACS Appl Mater Interfaces, Vol. 1, pp. 4-25.
- [7] Paunovic M., and Zeblicky R., (1985). 'Properties and structure of electroless copper', Plating and Surf. Fin., Vol. 72, pp. 52-54.
- [8] Shipley C.R., (1984), 'Historical Highlights of Electroless Plating', Plat. Surf. Finish, Vol. 71, pp. 92-99
- [9] Kuhn H.H., (1993), 'Characterization and application of polypyrrole-coated textiles', Intrinsically Conducting Polymers: An Emerging Technology', NATO ASI Series., Vol. 246, pp. 25-34.
- [10] Wang Xiao-li., Xu Bin-shi., Xu Yi., Yu He-long., Shi Pei-jing., and Liu Qian., (2005), 'Preparation of nano-copper as lubrication oil additive', J.Cent.South Univ., Vol. 12, pp. 203-206.
- [11] Wurtz A., (1844), 'Sur l'hydrure de cuivre', Ann. Chim. ET Phys., Vol. 3, pp. 11.
- [12] Weiskopf D.R., & Co., (1900), 'process for making copper mirror', D.R.P. No-124,710.
- [13] Chattaway F.D., (1907), 'Copper mirrors', Proc. Roy. Soc., London, 80-A, pp. 88-92.
- [14] Brenner A.R., and Riddell G.E., (1946), 'Nickel plating on steel by chemical reduction', J. Res. Natl. Bur., Vol. 37, pp. 31-34.
- [15] Narcus H., (1947), 'Practical copper reduction on nonconductors', Metal Finishing., Vol. 45, pp. 64-67.
- [16] Narcus H., Metal Finishing., Vol. 45, (1947), pp. 64-67.
- [17] Cahill A.E., (1957), 'American electrochemical society proceedings', Vol.44, pp. 130-135.
- [18] Zeblicky R.J., McCormack J.F., Williamson J.D., and Shneble F.W., (1963), U.S. Patent 3,095,309.
- [19] Copley, A.J. Mason, T.J. Saez, V. Review of effect of ultrasound on electroless plating processes, Trans. Inst. Met. Finish., 89, (2011), 303. 6.
- [20] Larson, C., Smith, J.R. Recent trends in metal alloy electrolytic and electroless plating research: A review, Trans. Inst. Met. Finish., 89, (2011), 333. 7.
- [21] Zhu, P., Wang, L.Y., Chen, Y., Zhou, M., Zhou, J. Electrodeposition of copper coating on AZ31 magnesium alloy, Surface Engineering, 28, (2012), 796. 8.
- [22] Schneider, M., Weiser, M., Dörfler, S., Althues, H., Kaskel, S., Michaelis, A., Electrodeposition of copper on aligned multi-walled carbon nanotubes, Surface Engineering, 28, (2012), 435. 9.
- [23] Wei, G.Y., Lou, J.W., Ge, H.L., Yu, Y.D., Jiang, L., Sun, L.X., Co-W films prepared from electroplating baths with different complexing agents, Surface Engineering, 28, (2012), 412. 10.
- [24] Yuan, X.L., Gao, J., Yang, Z.F., Wang, Z.X., Wang, Z.L., New electroless copper plating bath using sodium hypophosphite as reductant, Surface Engineering, 28, (2012), 377.
- [25] Pearlstein F., and Weightman R.F., (1973), 'Electroless copper plating using dimethylamine borane', Plating, Vol. 60, pp. 474-476.
- [26] Pearlstein F., and Weightman R. F., (1974.a), 'Electroless deposition of silver using dimethylamine borane', Plating, Vol. 61, pp. 154.
- [27] Pearlstein F., and Weightman R.F., (1974.b), 'Electroless cobalt deposition from acid bath', J. Electrochem. Soc., Vol.121, pp. 1023-1028.
- [28] Lowenheim F.A., (1974), 'Modern Electroplating', 3rd ed., Wiley, New York, pp. 636.
- [29] Mandich N.V., and Krulik G.A., (1993), 'On the mechanisms of plating on plastics', Plating and Surface Finishing., Vol. 80, pp. 68-73.
- [30] Deckert C.A., (1994), 'Electroless copper plating', Surface engineering, ASM Handbook, ASM International, Vol. 5, pp. 311- 322.
- [31] Deckert C.A., (1995.a), 'Electroless copper plating. A Review Part-1', Plating and surface finishing, Vol. 82, pp. 48.
- [32] Deckert C.A., (1995.b), 'Electroless copper plating-A Review: Part II', Plating and surface finishing, Vol.82, pp 58-64.
- [33] Pauliukait ĒR., Stalnonis G., Jusys Z., and Vaškėlis A., (2006), 'An EQCM study' Journal of Applied Electrochemistry, Vol. 36, pp. 1261-1269.
- [34] Regina Fuchs-Godec., Miomir G. Pavlović, and Milorad V. Tomić., (2013), Int. J. Electrochem. Sci., Vol. 8, pp. 1511-1519.
- [35] Balaramesh P., Venkatesh P., and Rekha S., (2014), Asian journal of science and technology., Vol.5, pp. 276-280.
- [36] Norkus E., Vaskelis A and Stalnioniene I., (2000), 'Changes of the Cu electrode surface area during the process of electroless copper plating', J. Solid State Electrochem., Vol. 4, pp. 337-341.
- [37] Pauliukait ĒR., Stalnonis G., Jusys Z., and Vaškėlis A., (2006), 'Effect of Cu(II) ligands on electroless copper deposition rate in formaldehyde solutions: An EQCM study' Journal of Applied Electrochemistry, Vol. 36, pp. 1261-1269
- [38] Regina Fuchs-Godec., Miomir G. Pavlović, and Milorad V. Tomić., (2013), 'The inhibitive effect of vitamin-C on the corrosive performance of steel in HCl solutions', Int. J. Electrochem. Sci., Vol. 8, pp. 1511-1519.
- [39] E.B. Saub ester, Plating, June (1972) 563.
- [40] J. Electron, M.S. Thesis, Univ. of Nancy (1960)

- [41] N. Feldstein and PR. Amodio, J. Electrochem. Soc., 117, (1970) 1110
- [42] M. Schlesinger and J.P. Marton, J. Phys. Chem. Solids, 29, (1967) 188.
- [43] J.P. Marton and M. Schlesinger, J. Electrochem. Soc., 115, (1968) 16.
- [44] Metal finishing Abstract, 12, No.6 (1970) 04.
- [45] Wein. S., "Copper films", PB 111237, OTS, US. Dept commerce (1953).
- [46] W.P.Innes, J.J. Grunwald, E.D.Ottavio, W.H.Toller ,C.Carmicheal,plating 56 (1996) 51.
- [47] C.F.Coomba,Printedcircuit Handbook,3rd ed.,McGraw-Hill,New York,1998,pp.12.1-45 and1301-18.
- [48] Ramasubramanian M., Popov B.N., White R.E., and Chen K.S. (1999). 'A mathematical model for electroless copper deposition on planar substrates'. J.Electrochem. Soc., Vol. 146, pp. 111-116.
- [49] Balaramesh P., Venkatesh P., and Abdul Jabbar A., (2014.e), 'Studies on stable Platinum (II) metal complexes of ethylenediamine and diethanolamine dithiocarbamates,' International journal of scientific and research publications., Vol. 4, pp.1-7.
- [50] Balaramesh P., Venkatesh P., and Abdul Jabbar A., (2014.f), 'Influence of dithiocarbamate on metal complex and thin film deposition', International journal of innovative research in science, engineering and technology., Vol.3, pp. 15301-15309.
- [51] Hung A., and Ohno I., (1985.a), 'Effect of pH on hypophosphite reduced electroless copper', J. Plat. Surf. Fin., Vol. 77, pp. 54-57.
- [52] Hung A., (1985.b), 'Effects of thiourea and guanidine hydrochloride on electroless copper plating', J. Electrochem. Soc., Vol. 132, pp. 1047-1049.
- [53] HungA., and Chen K.M., (1989), 'Mechanism of hypophosphite-reduced electroless copper plating', J. Electrochem. Soc., Vol. 136, pp. 72-75.
- [54] Wein S., (1959), Silvering process and materialsUS 2871139.
- [55] Saubestre E.B., (1962), 'Electroless plating today' Metal Finish., Vol. 60, pp. 17.
- [56] Saubestre E.B and Hajdu J.B., (1965), U.S Patent 3,460.952.
- [57] Saubestre E.B., (1972), 'Stability of electroless copper solutions'. Plating, Vol. 59, pp. 563-566.
- [58] Z.L. Wang, O. Yaegashi, H. Sakaue, T. Takahagi and S. Shingubara, J. Electrochem. Soc. 151 (2004) C781.
- [59] Ohno, O. Wakabayashi and S. Haruyama, J. Electrochem. Soc. 132 (1985) 2323.
- [60] Brookshire R.R., (1962), 'Method of copper plating by chemical reduction U.S. Pat. No., 3,046,159.
- [61] HonmaH.,andKobayashiT., (1994), 'Electroless Copper Deposition Process Using Glyoxylic Acid as a Reducing Agent', J. Electrochem. Soc., Vol.141, pp. 730-733
- [62] Bamberger,C.Schweitzer R., Chemikerzeitung,51,(1927) 212.
- [63] Eyber,G.,Chemiker Zeiting,51,4 (1927) 21
- [64] French E .A.,Trans.Opt.Soc.,25,(1923-24)229.
- [65] H.Nakahara, Printed circuit hand book,4th edition,C.F.Coombs,Mc Graw HILL Inc.,Newyork,1996.
- [66] Ohno I., Wakabayashi O., and Haruyama S., (1985), J. Electrochem. Soc., Vol. 132, pp. 2323-2330.
- [67] Meerakker J., van den E.A.M., (1981), Journal of Applied Electrochemistry., Vol. 11, pp. 395-400.
- [68] Meerakker J., van den E.A.M., and Bakker J.W.G. de, (1990). J. Appl.Electrochem., Vol. 20, pp. 85-90.
- [69] Duffy J., Pearson L., and Paunovic M., (1983), J. electrochem. Soc., Vol. 130, pp. 876.