AUTOCATALYTIC COPPER PLATING PROCESS ON NON CONDUCTING EPOXY RESIN PLATE

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Abstract :
Thin film nano coating of various materials are playing vital role in basic science and material science field. Typical nano metal plating of epoxy resin plate was studied by auto catalytic copper plating process using a chelating agent as poly hydroxylic alchohol, reducing agent as Dimethylamine Borane, stabilizer as cysteine and methionine. The electroless plating parameters such as P^H value of the plating solution, temperature and concentration of the bath composition should be closely maintained and monitored so as to get nanosized copper metal deposit. Crystal structure of the deposit was determined by X-RAY diffraction (XRD), Micro structural characteristics of solid object was examined by Scanning Electron Microscopy (SEM), Surface roughness of the copper deposit was analysed by Atomic Force Microscopy (AFM) respectively.

Index Terms - Chelating agent, Reducing agent ,Stabilizer, Dimethylamine Borane, Electro less .

Introduction:

Autocatalytic copper plating process has become a commonly used process in recent technology. This process provides nano sized particle deposition of pure metals , alloys or composites with uniform thickness and composition of thin layers of pure metals, on conductive and non - conductive substrates. Electroless plating of Nickel metal plays a vital role for the past 50 years and shows many commercial applications. Apart from Nickel the only other metal which is plated auto catalytically on a large scale is copper. Polymers are light in weight , reflectivity , good abrasion resistance , formability , high electrical conductivity, etc. Copper metallized polymer is used in electronic industry, pertroleum industry, air conditioning parts, multichip modules , computer body parts, decorative plastic industry etc. Metallization of polymer imparts abrasive nature, resistivity, electrical condutivity, wearability ,corrosion resistance, high impact resistance and weather proof .Due to the above attractive properties possibility of metallizing polymer has opened the new way to produce different materials [1]. Conductivity of non conducting material is enriched by Metalization process. The physical and mechanical properties of non conductive materials are also developed by metalization process. Different varities of polymers such as polypropylene, polythene , Teflon, polysulphone,epoxy polymer sheets , acrylonitrile, butadiene styrene etc. are metallized with Zinc, copper,Nickel,Gold,Silver,etc.[2,3]. Copper nanoparticle exhibits important physical and chemical properties which is not found in any other material. Because of its attractive features copper nano particles can be used in different types of fields like laboratory, industrial scale production , for example , manufacture of electrical and electronic devices.

Electroless plating is a cheapest and simple method , finds widest applications in the metal coating of polymer material .By this method a thin metallic layer will be developed on the activated polymer surface by oxi- reduction process without the application of any external power supply [4-7]. Electroless copper plating compositions are stable only upto certain period of time , after that which tends to decompose spontaneously. A small amount of copper nuclei generated in the bath composition initiates the random deposition, which decreases the bath stability and shortens the bath life. The monovalent copper oxide Cu_2O disproportionates to give metallic copper nuclei ,The incomplete reduction of bivalent copper ion ($Cu2^+$) and due to poor stability of the bath solution the quality of plated copper film decreases and observed dark colour apperance. In order to bring the stability of the plating bath some of the stabilizers are added. The structure of epoxy sheet is given below.

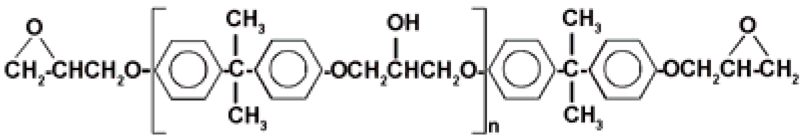


Figure 1.1 Structure of epoxy sheet.

This epoxy sheet is prepared by the condensation of epichlorohydrin and bisphenol- A . Molecular weight ranges from 350-8000. Electoless copper plating of an epoxy polymer sheet is an auto catalytic process in which plating bath composition is depending on i) Copper ions ii) Complexing agent iii) Reducing agent iv) P^H adjuster and v) Stabilizer .Traditional electroless copper plating technology has been used formaldehyde as reducing agent because of its low cost and high quality of the deposition , but which is not environmentally friendly[8] and also high P^H is required. Now a days the society is paying more attention for the protection of environment. Therefore non- formaldehyde electroless plating is preferred over formaldehyde reducing agent. In recent years toxic formaldehyde will be replaced by glyoxylic acid [9,10], hypophosphite [11-14], sodium bisulfate,sodium thiosulfate pentahydrate ($Na_2S_2O_3.5H_2O$) [15] and Dimethylamineborane [16,17].

To discuss in more detail, the electroless nano deposition is a self-initiating, autocatalytic process in which the catalytically active surface is immersed in a solution containing complexed metal ions and a reducing agent dimethyl amine borane .The role of reducing agent is to convert the metal ions to non- valent metal on the surface to form a continuous uniform metal film (Ohno I., 1991). The driving force is an auto catalytic redox reaction on the pretreated catalytic surface. The epoxy polymer surface is activated by $PdCl_2$.

Table 1.1 Differences between the properties of electroplating, electroless plating and immersion plating

Property	Electroplating	Electroless plating	Immersion plating
Driving force	External power	Auto catalytic redox reaction	Chemical displacement
Cell reaction	$M_{(A)} \rightarrow M_{(C)}$	$M^{2+} + R \rightarrow M + O$	$M^{n+} + M_1 \rightarrow M + M_1^{n+}$
Anode reactant	M or H_2O	R, Reducing agent in solution	M_1, dissolving metal
Nature of deposit	Pure metal or definite alloy	M contaminated by O/R derived species	Pure metal (porous and poorly adherent)
Thickness limit (μm)	1-100	1-100	< 10

This work is an cost effective, ecofriendly process was used to deposit copper on the activated surface of the epoxy resin plate by auto catalytic method using a reducing agent Dimethyl amine borane (DMAB) and stabilizers as selective natural aminoacids of cystein and methionine .The deposition rate of copper carbonate in plating bath on micro structure and changes in physical and mechanical properties of copper plated epoxy resin plates were characterized by X-ray diffraction , Scanning electron microscopy and Atomic force microscopy techniques.

Table 1.2
Major components of an electroless copper plating bath

S.No.	Nature of the compound	Functions	Examples
1	Coating solution	Soluble salts of metal like chlorides and sulphates to be plated.	CuSO4,CuCo3,$CuCl_2$ etc.
2	Complexing agent	To improve the quality of deposit	EDTA,Citrate, D-Mannitol, Saccharose,Xylitol etc.
3	Reducing agent	To reduce the metal ions into metal	Formaldehyde, hypophosphite, DMAB, Glyoxalic acid etc.
4	Stabilizer	To prevent the decomposition of the plating bath	2,2’-Dipyridyl, Pyridine,Aminoacids benzotriazole etc.
5	*p*H adjuster	To maintain the required *p*H throughout the experiment	NaOH, KOH, NH4OH etc.

Experimental Details

The following compounds of A.R grades were used in the present study.

1. Copper carbonate
2. Methane Sulphonic acid
3. Dimethyl amine borane
4. Xylitol
5. Cystein
6. Methionine

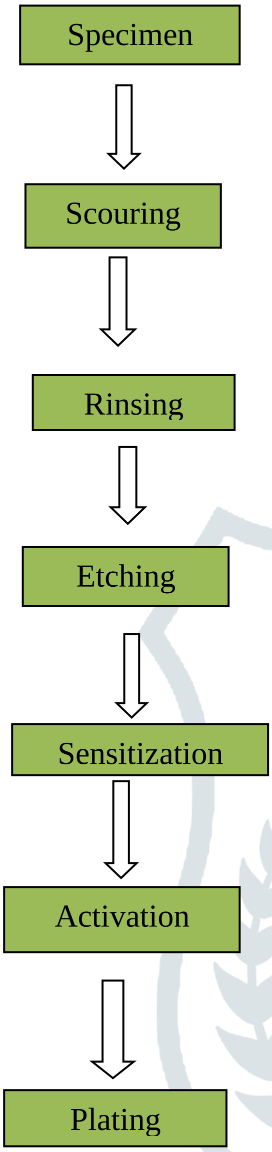
$$Metal\ ion + Reducing\ agent \rightarrow \underset{(Deposited)}{Metal} + Oxidized\ \ product$$

Table 1.3
Bath compositions of copper methanesulphonate Xylitol plain bath with stabilizers Cystein and Methionine Stabilizers

Bath contains	Xylitol			
	Plain Bath	Cystein Stabilizer Bath	Plain Bath	Methionine Stabilizer Bath
CuMS(II)ion containing salt	3g/L	3g/L	3g/L	3g/L
Xylitol	20g/L	20g/L	20g/L	20g/L
DMAB	5 g/L	5 g/L	5 g/L	5 g/L
KOH(P^H)	10.5 ± 0.25	10.5 ± 0.25	10.5 ± 0.25	10.5 ± 0.25
Temperature	28 ± 2°C	28 ± 2°C	28 ± 2°C	28 ± 2°C
Stabilizers	0ppm	1ppm	0ppm	1ppm

SFigure 1.2

Steps to carryout Electroless copper plating



In this present work , the following two electroless copper baths were prepared by using an ecofriendly chelating agent polyhydroxylic alcohol Xylitol and two natural sulphur containing aminoacids like cystein and methionine. Xylitol containing copper methane sulphonate bath was used instead of copper carbonate and Dimethylamine Borane was used as the reducing agent in the bath. KOH was used to stabilize and optimize the bath in alkaline medium at P^{H}>10.5 . Cysteine and Methionine were tried in Xylitol bath and the effect of bath conditions ,rate of deposition and various properties were studied.

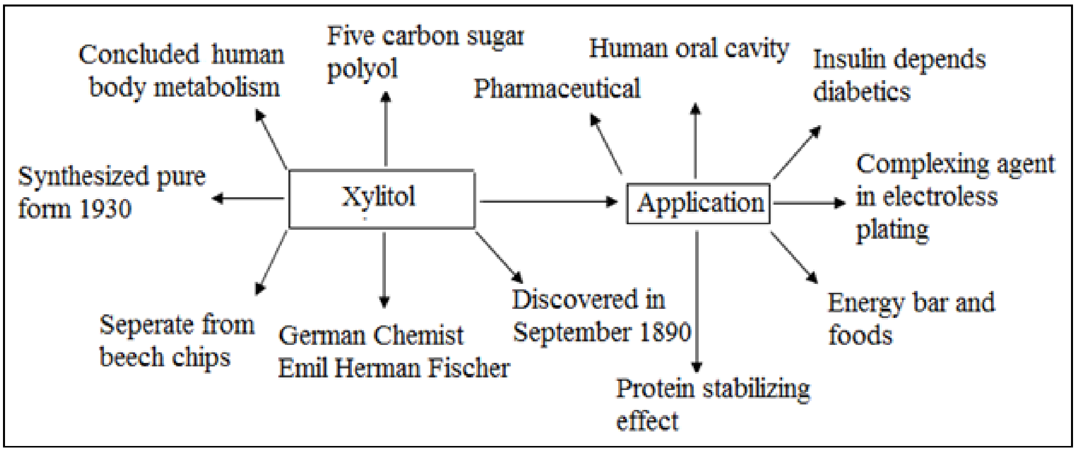


Figure 1.3 Flow chart for xylitol and its applications

The effect of above two stabilizers cystein and methionine in Xylitol containing methane sulphonate and Dimethyl amine borane based optimized bath at P^H 10.5 was studied . Using XRD the orientation of the crystal and lattice parameters were studied . There are three major reflection planes (111) ,(200) , and (200) were studied by this work. In general Copper films had a strongly preferred orientation of (111) because of the lowest surface energy. According to the Lee et al., report copper methane sulphonate bath produces large number of copper ions ,because of the high conductivity and solubility leading to (200) plane.

Crystal structure analysis by XRD

Crystal structure of the copper deposits are experimentally determined by XRD technique (West A . R .1974) and identification of unknown materials , atomic spacing , single crystal orientation , preferred orientation of polycrystals , stresses , lattice constants and geometries (Guo D.etal,2006,Junginger R , et al , 1988, Lee D N , 1999,Swanson H.E, et al,1953a,Swanson H E , et al , 1953 b, Warren B E , 1969),etc.

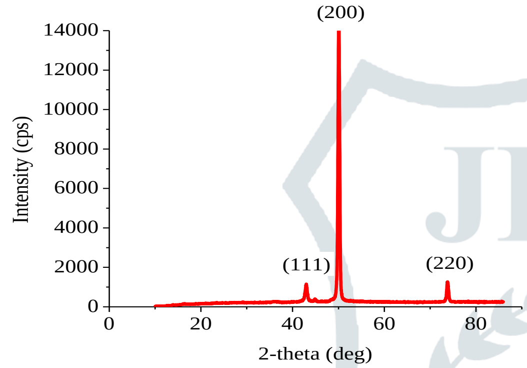


Figure 1.4 XRD pattern of copper deposits on methanesulphonate xylitol plain bath

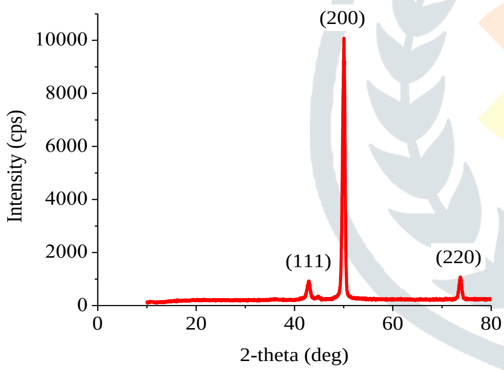


Figure 1.5 XRD pattern of copper deposits on methanesulphonate xylitol plain bath with cystein (1ppm)

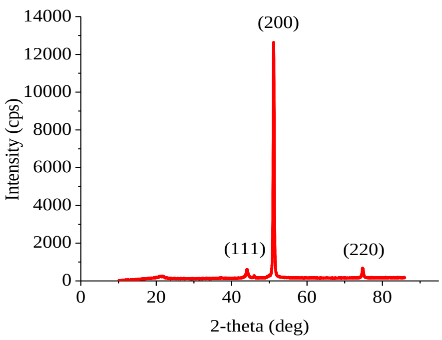
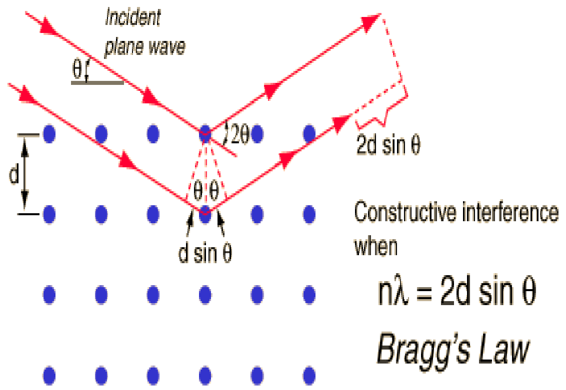


Figure 1.6 XRD pattern of copper deposits on methanesulphonate xylitol plain bath with Methionine (1 ppm)

The wavelength of electromagnetic radiation to the diffraction angle and the space lattice in a crystal sample was calculated by Braggs' law



. Where 'd' is the spacing between atomic planes in the crystalline phase and 'λ' is the wavelength and 2θ is the angle detected. The percentage of intensity is obtained by measuring the full width half maximum (FWHM).The crystallite size is calculated by Debye – Scherrer equation.

$$D = K \lambda / \beta_{rad} \cos\theta$$

where K is the Scherrer constant, λ is the wavelength of light used for diffraction, β is the Full Width Half Maximum'(rad) of the sharp peaks and θ is the angle measured. The Scherrer constant (K) is the shape of the particle and has the value 0.89.Specific surface area of the copper deposit is determined by the formula

$$S = \frac{6\times10^3}{d\,D}$$

Where D is the crystallite (nm) and d is the theoretical density of copper (8.96 g/cm^{-2})

The major applications of XRD are

i) Non – destructive technique ..
ii) Identification of compounds and quantification of concentration of phases.
iii) Determination of atomic arrangement.
iv) Measurement of thickness of thin film and multifilms orientation of grains.

Surface morphology of copper deposits by SEM analysis

The two dimensional structure of deposited copper was studied by SEM analysis. The surface morphology of copper deposit was studied by scanning electron microscopy (SEM) analysis at magnification of x 2000 and x 5000 for the specimen used in plain bath and additive baths. Figure 1.5 shows that regular and fine grained copper deposits were obtained when the additives were added to the Xylitol bath. Addition of small volume of stabilizers not only stabilizes the bath and also changes the physical features such as colour, shape and crystallite size of the copper deposits. Many interesting shapes like flower, honey comb, rock, needle and pyramid etc. were observed.

The copper deposits obtained in the plain Xylitol bath was sand-like in morphology, but, in the presence of stabilizers, rock like, cauliflower, honey comb etc. structures deposits were formed.The study shows that addition of stabilizers increases the coating and modifies the physical properties of the copper deposits compared to other plain baths.

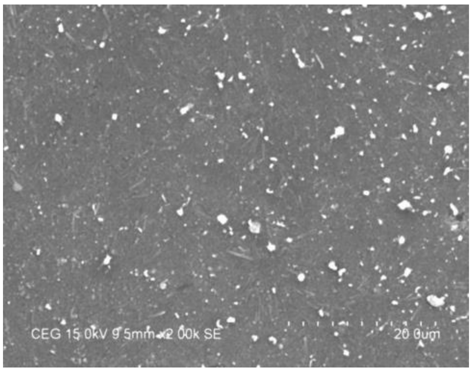


Figure 1.5 SEM images of copper deposits on methanesulphonate Xylitol plain bath with cystein magnification 2000

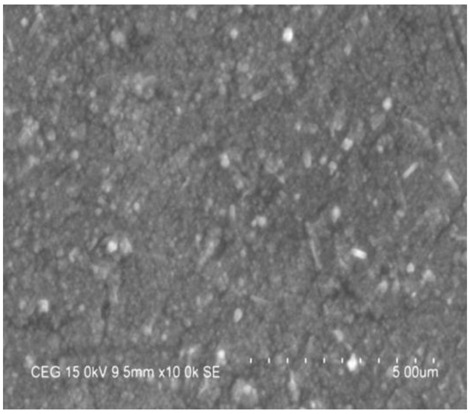


Figure 1.6 SEM images of copper deposits on methanesulphonate Xylitol plain bath with cystein magnification 5000

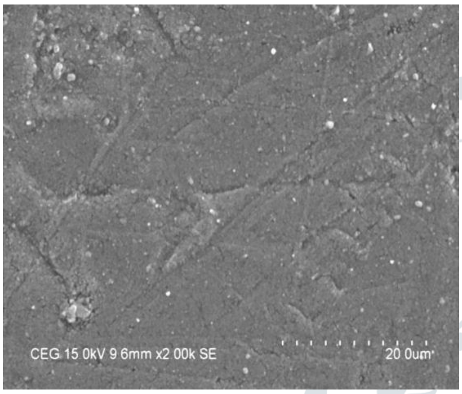


Figure 1.7 SEM images of copper deposits on methanesulphonate Xylitol plain bath with methionine magnification 2000

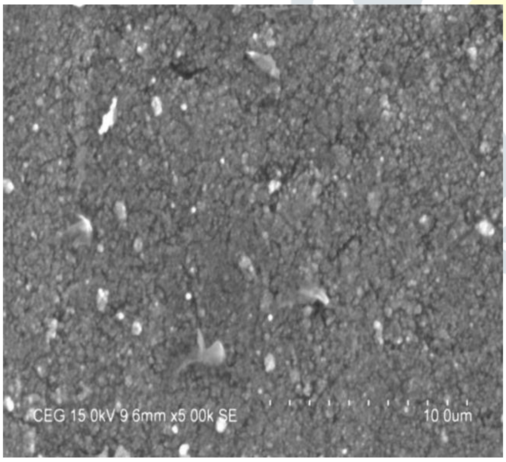


Figure 1.8 SEM images of copper deposits on methanesulphonate Xylitol plain bath with methionine magnification 5000

Surface morphology of copper deposits by AFM analysis

Based on Atomic force microscopy (AFM) studies, the bright appearance of copper deposits usually indicates better mechanical and physical properties. Roughness value is inversely propositional to smooth deposition. The xylitol plain bath produces the maximum roughness value 397 nm. The roughness values decreased due to the addition of cystein and methionine. The smooth and compact coatings as evidenced by their lower roughness values in Xylitol plain bath.

The deposits were dark brown in color for Xylitol baths without stabilizers. However, on addition of stabilizers, the deposits become semi bright with cystein and methionine images of, (a) topography of copper deposits, (b) 3-D image and (c) surface area shows that the roughness of the deposits.

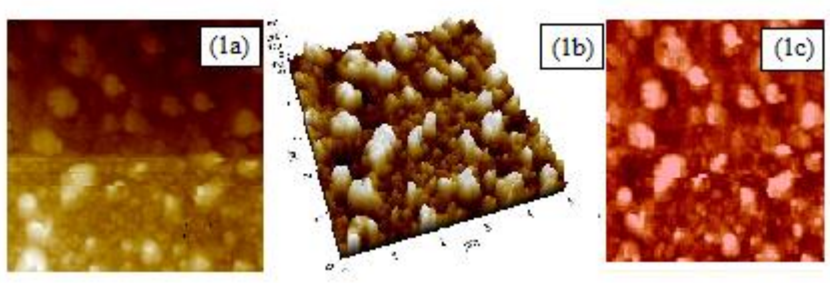


Figure 1.9 AFM images of copper deposits on methane sulphonate Xylitol plain bath with Cystein (1ppm); (a) surface area (b) 3D image (c) topography of copper deposits.

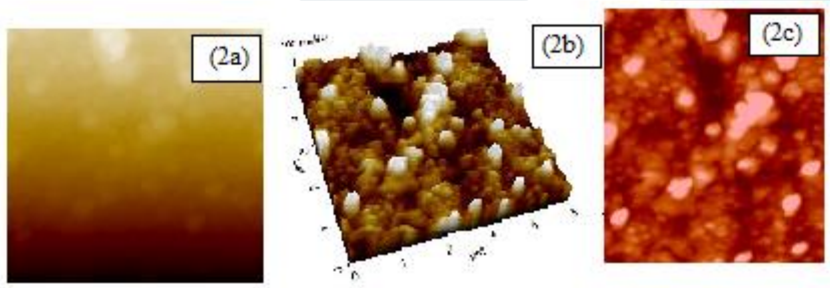


Figure 2.0 AFM images of copper deposits on methane sulphonate Xylitol plain bath with Methionine (1ppm); (a) surface area (b) 3D image (c) topography of copper deposits.

Table 1.4 Roughness value and shape of copper deposits on Xylitol methanesulphonate plain bath with stabilizers from AFM studies.

S.No	Xylitol plain bath with stabilizers (1 ppm)	Roughness value (nm)	Shape or stucture
1	Plain bath	397	Grains
2	Cystein	142	Pyramid
3	Methionine	156	Gravels

Conclusion

An eco- friendly poly hydroxylic compound xylitol was used as a complexing agent in copper methane sulphonate bath. The xylitol bath was optimized at a pH of 11.5 ± 0.25 and using KOH solution . Cystein and methionine were used as the stabilizer in the xylitol contained baths. The surface studies of the electroless bath reports the copper deposits of xylitol and cystein containing bath results in coarse grained deposits while that of the xylitol in methionine containing baths are fine grained with uniform distribution

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