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Studies of role of additives on electroless copper methane sulphonate an eco-friendly green bath

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The electroless copper deposition from copper methane sulphonate bath is carried out. The bath consists of copper methane sulphonte, EDTA, *p*-formaldehyde and base to raise the pH as the coating is pH sensitive. In recent years methane sulphonic acid is gaining importance among researchers due to its properties like less toxicity and easily biodegradable than other mineral acids. The role of stabilizers like 2MBT, imidazole, 1,2,4-triazole, 1,2,3-benzotriazole are investigated. The effectiveness of stabilizers is primarily studied by gravimetry method and confirmed by cyclic voltammetric studies. The surface morphologies of copper deposits were studied by SEM and XRD.

Keywords: Copper electroless deposition, additives, stabilizer, surface morphology, benzotriazole.

Introduction

Electroless coating is an established technology past a few decades. It is a method of coating of fine film of metals in microns and other compounds employed in different industrial and other electronic applications. The coating of exquisite noble metals like gold and silver has been used in early history. Wurtz is the person who first discovered electroless coating of nickel using hypophosphite[1] as a reductant in the year 1844.

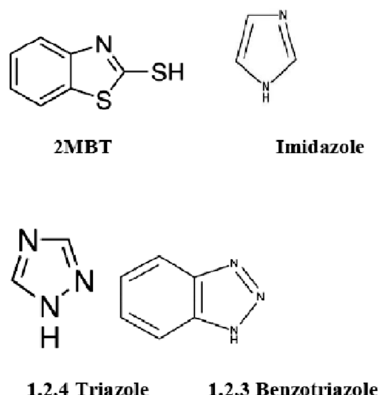
In 1946, Brenner and Riddell advanced the method and have suggested the working environment for the coating of nickel[2,3] without electricity and with the help of reducing agent. The incorporation of reducing agents like sodium hypophosphite is to obtain precise nickel plating. The term 'Electroless' was coined by William Blum[4] for this auto-catalytic method as this technique does not require the supply of electricity for the process to take place. In this coating procedure, a highly nobel metal[5,6] is coated from its electrolytic plating solution on a surface which is activated by a catalyst of a less noble metal in the presence of reducing agent which provides the necessary electrons for reduction and the metal deposition over the substrate takes place. Electroless plating finds application in the field of printed circuit boards, integrated circuits fabrication and in electromagnetic interference shielding[7]. On the other hand electroplating involves external electric current to reduce the metal cations to form a metal coating on the electrode. The reaction of electroless plating can be shown below:

Metal ion + Reducing agent →

Deposited metal atom + Oxidized product

In a well established method a major challenge is to retain conventional processing, with aqueous solutions and existing process with cost-effective, 'green' electrolytes. Using biodegradable electrolytes based on methanesulfonic acid[8] (MSA) which has good electrolytic conductivity and is capable of dissolving many metals. In this paper, electroless plating of copper is investigated with copper methane sulphonate salt. The bath consist of other ingredients viz. EDTA as complexing agent, *p*-formaldehyde as reducing agent at pH 13[8,9]. pH 13 is the optimum pH at which the bath gives maximum rate of deposition with good bath stability. Above13 pH bath is observed to decompose as recorded in our earlier work[8]. Hence a pH of 13 is chosen for further studies. The effects of additives like 2MBT[10,11], imidazole[12,13], 1,2,4-

triazole[14], 1,2,3-benzotriazole[12,13] on electroless copper plating were studied initially by gravimetric methods and the role of additive is analyzed by cyclic voltammetric technique.



Structure of stabilizers

Experimental

Eco-friendly methane sulphonate plating bath:

In the preparation of both electroless as well as electroplating MSA baths are getting more attention. Procell *et al.* discovered that methane sulphonic acids produces apparent solution as it can form extremely dissolvable metal salts in water[15,16]. MSA based baths become more popular in the early 1980's for various plating baths containing metal has been found to be an excellent medium for solubility of metal salts and appear to be the best option for different plating applications[5,17–22]. It is easy to handle methane sulphonic acid as liquid and can be recyclized. It is biodegradable forming sulphate and CO_2. Methane sulphonic acid is found to be an eco-friendly product and also considered as a component of the natural sulphur. It is less corrosive and toxic than other mineral acids[23].

MSA baths works well at room temperature with excellent bath life, conductivity and biodegradability[21,22], hence found to be more superior over other plating baths.

Plating bath composition:

The bath is prepared with AR grade chemicals and all the solutions were prepared with double distilled water. A new electroless copper methane sulphonate bath was prepared and is more advantageous than normal conventional bath. The plating bath consists of the following constituents:

1. Cu methane sulphonate	- 12.027 g/L
2. EDTA	- 20 g/L
3. *p*-Formaldehyde	- 10 g/L
4. pH	- 12.5 to 13.0
5. Temperature	- Room temp.
6. Additives	- 1 ppm

The weight gain experiments of electroless plating process has been conducted in a beaker containing 100 ml of plating solution with 2.5×2.5×0.1 cm^3 copper sheets (purity 99.99%). By using weight gain method the rate of electroless copper deposition were estimated.

The deposition rate was obtained using the following formula:

$$\text{Rate of deposition } (\mu/h) = \frac{W \times 60 \times 10^4}{DAt}$$

W = deposit weight (g)

D = density of the deposit (g/cm^3) (density of copper = 8.96 g/cm^3)

t = deposition period (h)

A = plating area (cm^2)

Pretreatment and plating procedure:

High purity copper substrates were polished with abrasive sheet, degreased and activated in a solution of 0.1 g/L acidic $PdCl_2$ for 30 s. The substrate surface is cleaned with double distilled water, dried, weighed and immersed in 100 ml of electroless plating solution for half an hour. On immersion the plating is observed to begin in 30 s with the evolution of hydrogen bubble from the plating surface. The experiment was carried out at a room temperature of 28°C (±0.5°C). After plating the substrate is thoroughly cleaned with double distilled water and the panel is dried out. The panel is reweighed to calculate the weight of the deposit.

Cyclic voltammetric studies:

Cyclic voltammetric curves were obtained by standard electrochemical analyzer CHI 760C. Cyclic voltammetric studies were carried out with three electrode assembly. The working electrode is 1 cm^2 in area of copper electrode. The counter electrode is 1 cm^2 platinum foil and standard calomel electrode is used as the reference electrode. A potential window

of –1.4 to 0.4 V at scanning rate of 50 mV/s was kept constant for all the experiments.

Evaluation of electroless copper thin film:

The crystal orientation, its size and the quality of the deposited copper plate were found using X-ray diffraction patterns. The topography of the copper surface was evaluated using Scanning electron microscope (S-3000) of magnification x500 and x1000.

Results and discussion

Gravimetric/Weight gain method:

The rate of electroless copper deposition, in the presence and absence of additives, was determined using weight gain method, which is shown in Table 1. In this present study the role of azole compounds are examined. Azole compounds were found to be an important inhibitor for corrosion which has gained attention among many researchers[24,25]. Azoles are a class of five membered heterocyclic compounds containing compulsorily a nitrogen atom and along with element like sulphur, oxygen or nitrogen as a component of the ring[26] containing organic compounds. This N atom acts as electron donars and increases chemisorption on the surface of the metal[27–29]. Additionally due to the interaction with the conjugation of rings and this causes the inhibition in deposition[30] process. From Table 1, it is very clear that additive free bath show a greater deposition rate but the bath shows less stability. It was observed from the rate of deposition that the stabilizers 2MBT, imidazole, 1,2,4-triazole and 1,2,3-benzotriazole inhibit the rate of deposition and enhances the bath stability. Hetero atoms like nitrogen and sulphur[31] having delocalised π-electrons gets easily adsorbs on the surface of the copper which slows down the deposition of copper on to the surface and also improves the quality of deposits in terms of good adherence and brightness of the deposits. All the additives show stabilizing property in which 2MBT shows high rate of inhibition, which may be accounted for the high affinity of copper for sulphur that provides stronger coordination with the surface of copper[10].

Cyclic voltammetry:

Cyclic voltammetric techniques[32–34] is helpful to identify the mechanism of copper plating process and helps to study the impact of the additives in plating process. The reaction of the electroless process occurs at the electrode-electrolyte interface and can be measured by the cathodic and anodic reaction viz. the reduction reaction leading to deposition of copper and the reducing agent gets oxidized respectively. Therefore, it is helpful to study the effect of additives on the anodic and cathodic reactions in the copper methane sulphonate bath with *p*-formaldehyde as reducing agent. Cyclic voltammogram for the copper plating bath containing various additives like 2MBT, imidazole, 1,2,4-triazole and 1,2,3-benzotriazole and in the additives free bath were examined at 50 mV/s between 0.4 and –1.4 V (vs SCE) by employing copper as working electrode.

Fig. 1 shows the cyclic voltammogram of the additive free bath i.e. without any additive. The cathodic scan showed two peaks at –0.39 V and –0.8 V. The cathodic peak at –0.39 V is small and is due to the reduction of cuprous ion to copper atom and the second cathodic peak[35–38] is large due to the reduction of cupric ion and cuprous ion to copper atom. In the reverse scan –0.26 V, –0.12 V is anodic oxidation of Cu(0) to Cu(II) and formaldehyde oxidation to formate, two peaks are merged.

The cyclic voltammogram of the above bath with various additives are taken and the oxidation potential of formaldehyde is given in Table 2. Additives used shows slight nega-

Table 1. Deposition rate of copper deposits on optimized methane sulphonate EDTA plain bath with stabilizers

Sl. no.	Stabilizers	Rate of deposition in μm/h for 1 ppm	Stability of the bath
1.	Additive free bath	3.5	Less stable
2.	2MBT	2.2	Stable
3.	Imidazole	2.9	Stable
4.	1,2,4-Triazole	2.6	Stable
5.	1,2,3-Benzotriazole	2.4	Stable

Table 2. Oxidation peak current and peak potential values from Cyclic voltammogram of electroless copper-EDTA bath for stabilizers (1 ppm)

Sl. no.	Stabilizers	Peak current (mA)	Peak potential (mV)
1.	Stabilizer free bath	0.00406	–0.26
2.	2MBT	0.00246	–0.368
3.	Imidazole	0.00314	–0.419
4.	1,2,4-Triazole	0.00282	–0.377
5.	1,2,3-Benzotriazole	0.00266	–0.364

tive shift in anodic peak potential and low anodic peak current values which is due to the adsorption of additives to the plating surface there by slowing down the process, which confirm the stabilizing property[39] of the additives used as shown in Fig. 1 to Fig. 5.

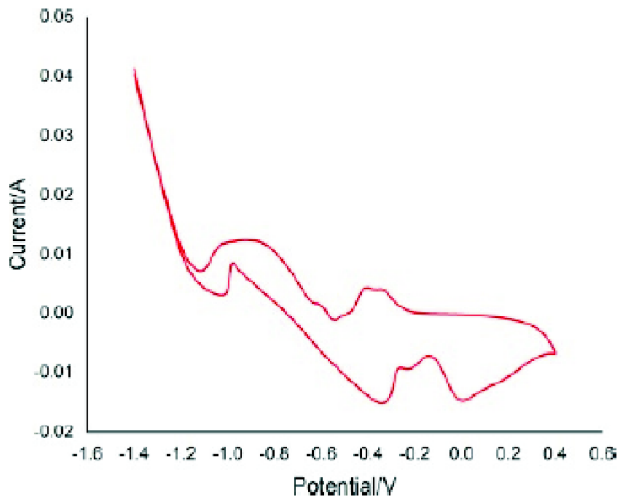


Fig. 1. Cyclic voltammogram for copper methane sulphonate EDTA plain bath at pH 13.

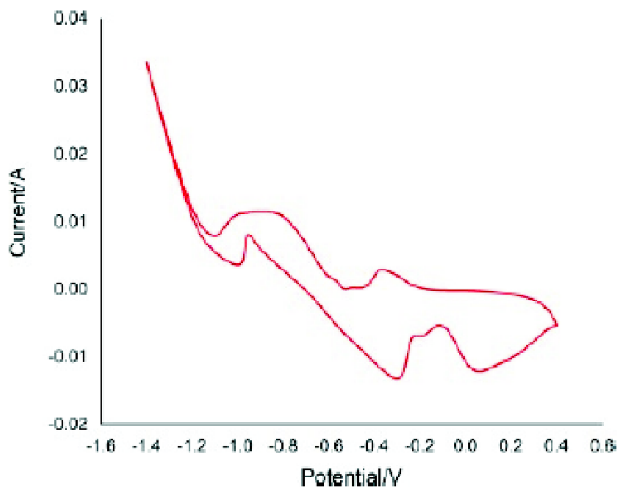


Fig. 2. CV for electroless copper methane sulphonate EDTA plain bath with 2MBT (1 ppm) at pH 13.

From the cyclic voltammogram graph (Fig. 1) for stabilizer free bath shows 0.00406 mA as oxidative peak current for formaldehyde. Imidazole shows a peak current 0.00314

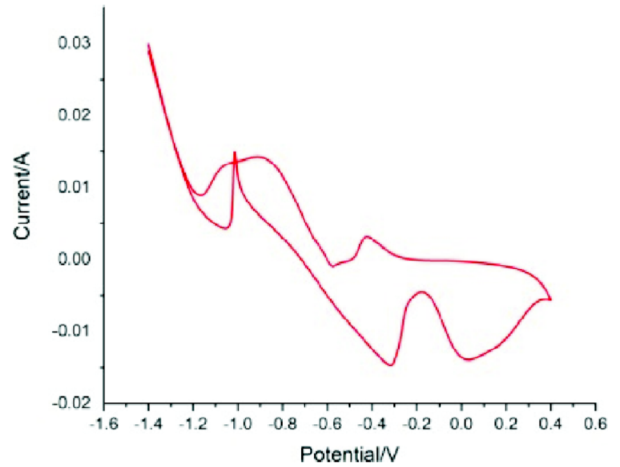


Fig. 3. Cyclic voltammogram (CV) for copper methane sulphonate EDTA additive free bath with imidazole (1 ppm) at pH 13.

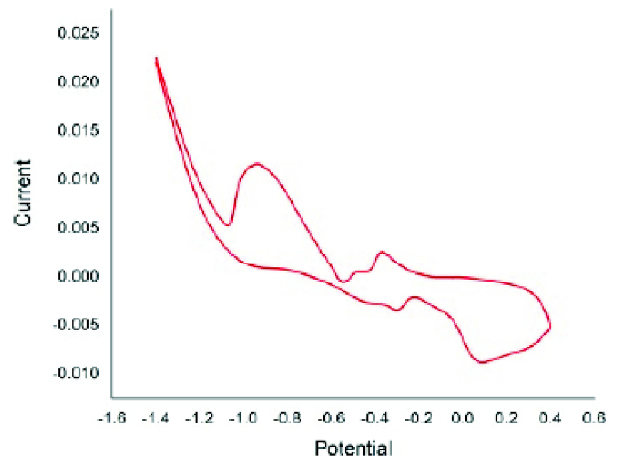


Fig. 4. CV of copper methane sulphonate EDTA plain bath with 1,2,4-triazole (1 ppm) at pH 13.

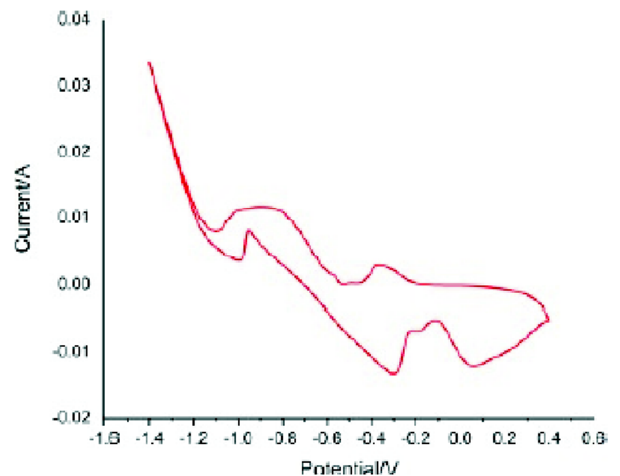


Fig. 5. CV for electroless copper methane sulphonate EDTA stabilizer free bath with 1,2,3-benzotriazole (1 ppm) at pH 13.

mA representing the inhibition of the deposition rate by inhibiting the oxidation of formaldehyde process, which results in lower rate of copper reduction and thus stabilizing the bath. 1,2,4-Triazole[40] having three N atom shows better stability than imidazole having two N atom. The adsorption of molecule on surface is due to the lone pair of electrons from the hetero atom (N) and double bonds in the compound.

Benzotriazole[41] having an aromatic ring enhances the adsorption property along with the lone pairs of electrons of three N atoms of compound thus stabilizing more effectively. In 2MBT structure two nitrogen atoms is replaced by S atom, the combination of nitrogen and sulphur atom[42] behaves as a best inhibitor, retarding the process by adsorption. Thus the trend of stabilization in increasing order is:

Imidazole < 1,2,4-triazole < benzotriazole < 2MBT

XRD:

The preferred orientation of XRD from literature for thin film of copper corresponds to different diffraction peaks observed at (111), (200), (220) and (311) at 2θ values of 43.3°, 50.4°, 74.1° and 89.9°, respectively, according to JCPDS ref. 004-0836[43]. The XRD patterns obtained in this EDTA bath well correlates with the XRD pattern obtained for copper film according to JCPDS ref. 004-0836. It is noted that anyone of the above said plane will be taken as the preferred plane in the presence of additives. From the XRD pattern given in Fig. 6 to Fig. 10 it is well understood that the ideal orientation is 200 for copper methane sulphonate bath irrespective of the additives added. The film formed is merely copper metal and copper oxide was not formed in this deposit.

The effective crystalline size of the thin film of the deposited copper has been calculated by using Scherrer's equation[8,44,45]:

$D_{hkl} = K.\lambda/\beta \cos\theta$

where

λ – Wavelength of light used for diffraction (i.e.) (1.5418 Å)

β – Full width half maximum (rad) of sharp peak

θ – Bragg's angle measured

K – Scherrer constant (0.89).

The crystalline size of copper deposits for the stabilizer free bath and bath with stabilizer was represented in Table 3. The intensity count for the ideal orientation (200) plane in the stabilizer free bath is 13516 counts and crystalline size is 54.59 nm. From the above table it is noted that 1,2,4-triazole shows the smallest count of intensity showing more arbitrary orientation within the stabilizers. Imidazole possess the maximum intensity count of 15795 count presenting the ideal orientation of (200).

Table 3. Crystallite size of copper deposit with 1 ppm of stabilizers with formaldehyde as reducing agent

Sl. no.	Additives	Crystalline size (nm)
1.	Additive free bath	54.59
2.	2MBT	61.04
3.	Imidazole	83.33
4.	1,2,4-Triazole	70.59
5.	1,2,3-Benzotriazole	60.89

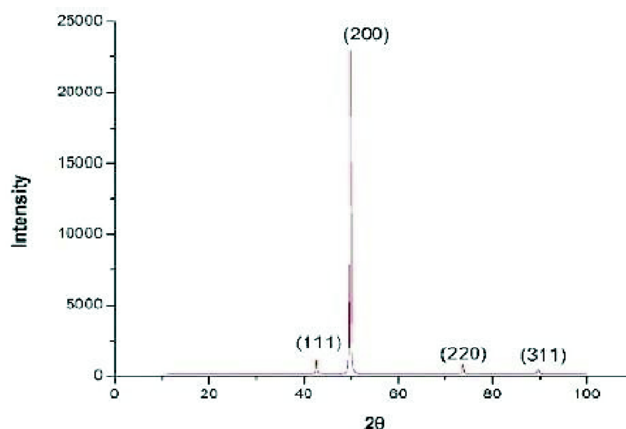


Fig. 6. XRD images of copper deposits in EDTA plain bath (1 ppm).

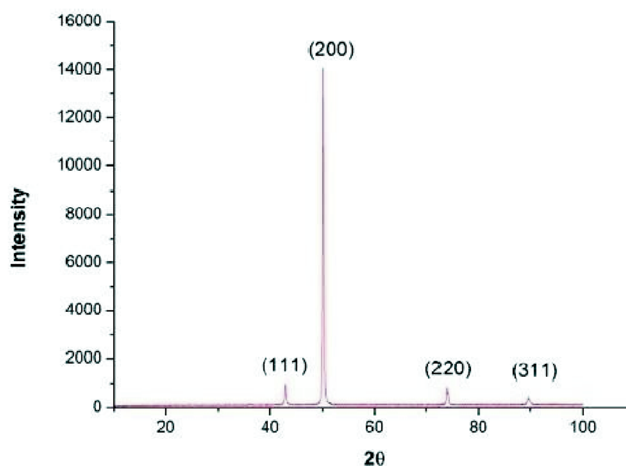


Fig. 7. XRD images of copper deposits in EDTA bath with 2MBT (1 ppm).

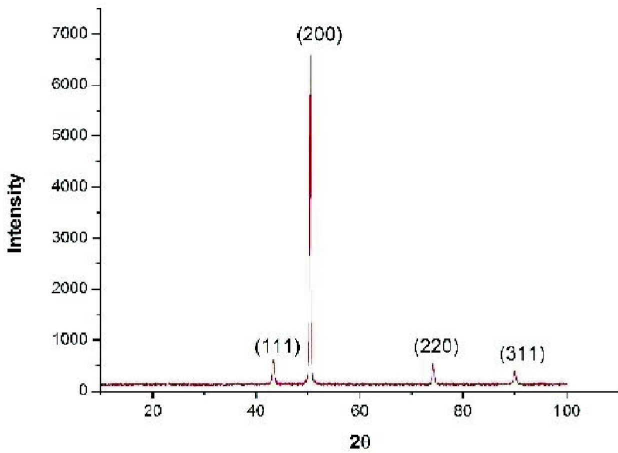


Fig. 8. XRD images of copper deposits in EDTA bath with 1,2,3-triazole (1 ppm).

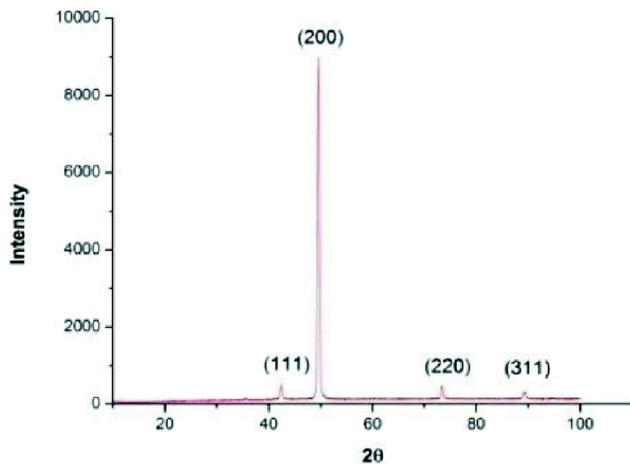


Fig. 9. XRD images of copper deposits in EDTA bath with 1,2,3-benzotriazole (1 ppm).

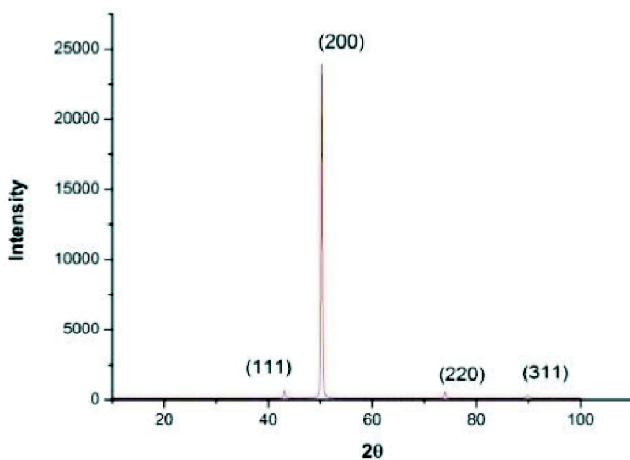


Fig. 10. XRD images of copper deposits in EDTA bath with 1,2,3-imidazole (1 ppm).

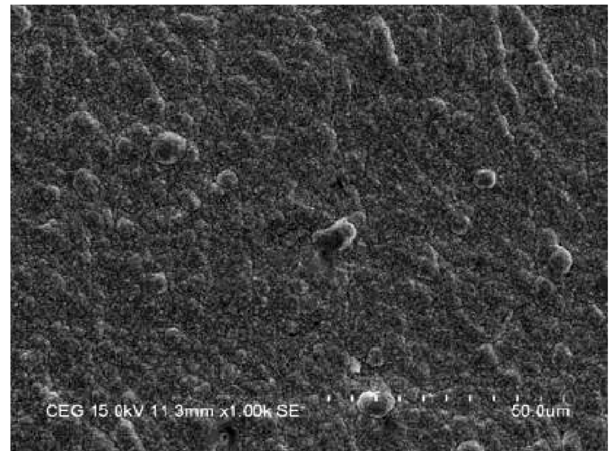


Fig. 11. SEM images of electroless copper deposit of stabilizer free bath at a magnification of x1000.

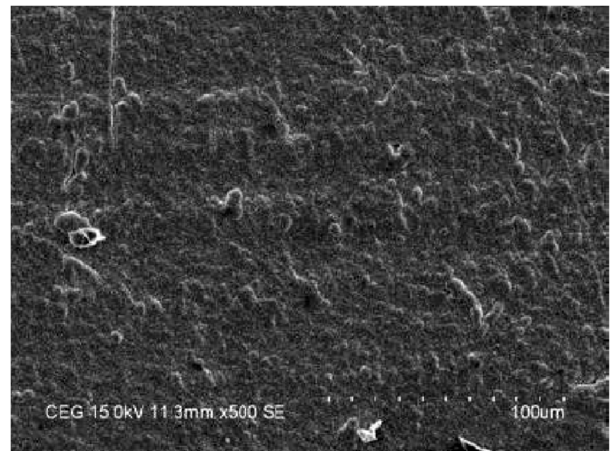


Fig. 11a. SEM images of electroless copper deposit stabilizer free bath at a magnification of x500.

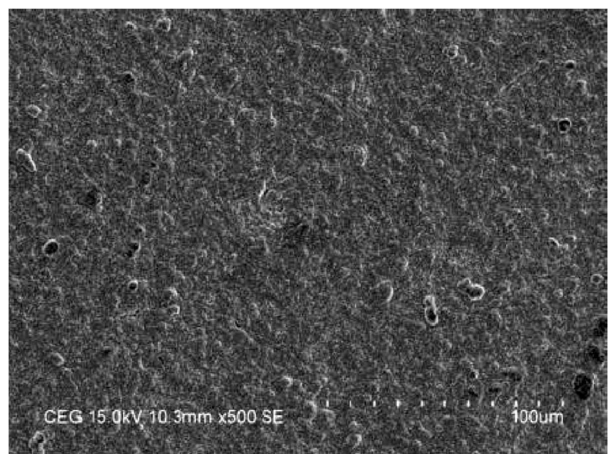


Fig.12. SEM images of electroless copper deposit of 2MBT at a magnification of x1000.

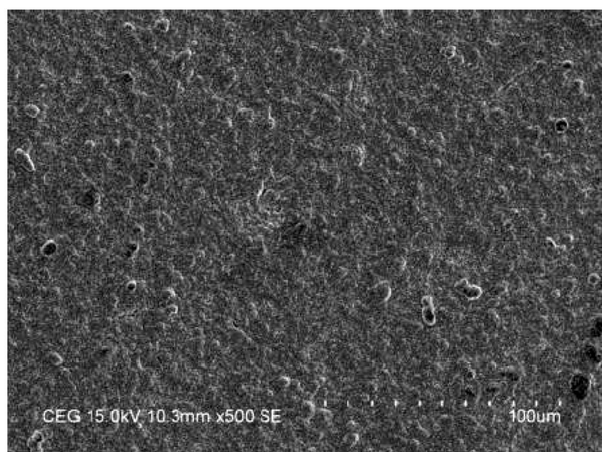


Fig. 12a. SEM images of electroless copper deposit with 2MBT at a magnification of x500.

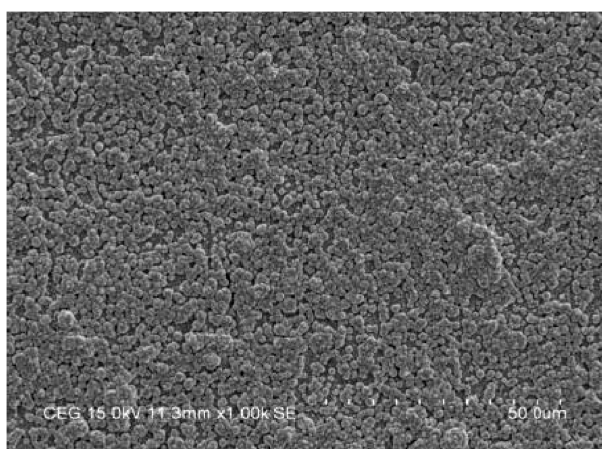


Fig. 13. SEM images of electroless copper deposit with imidazole at a magnification of x1000.

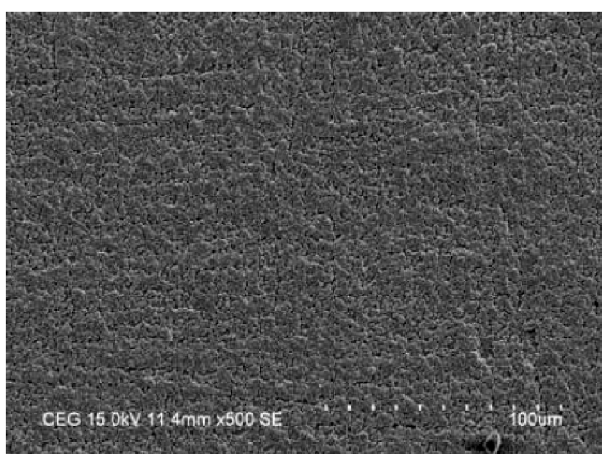


Fig. 13a. SEM images of electroless copper deposit with imidazole at a magnification of x500.

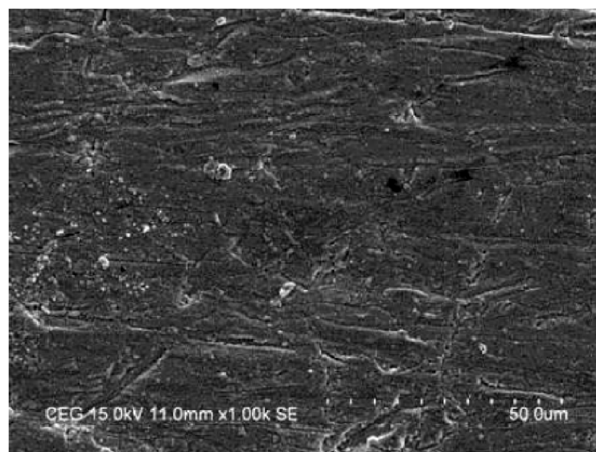


Fig. 14. SEM images of electroless copper deposit with 1,2,4-triazole at a magnification of x1000.

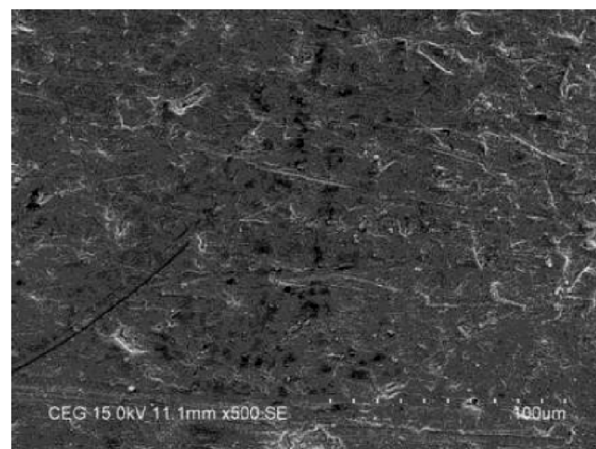


Fig. 14a. SEM images of electroless copper deposit with 1,2,4-triazole at a magnification of x500.

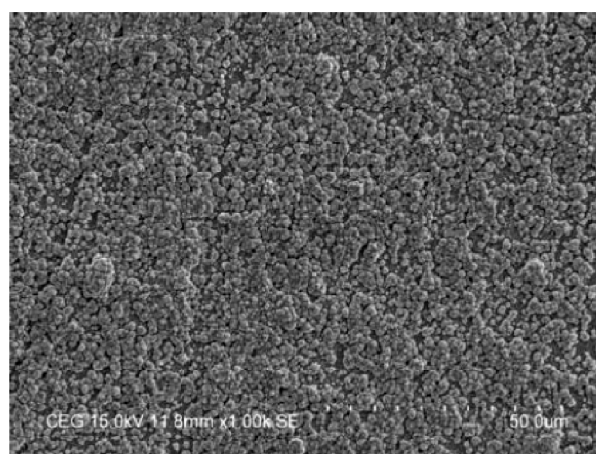


Fig. 15. SEM photograph of electroless copper deposit with 1,2,3-benzotriazole x1000.

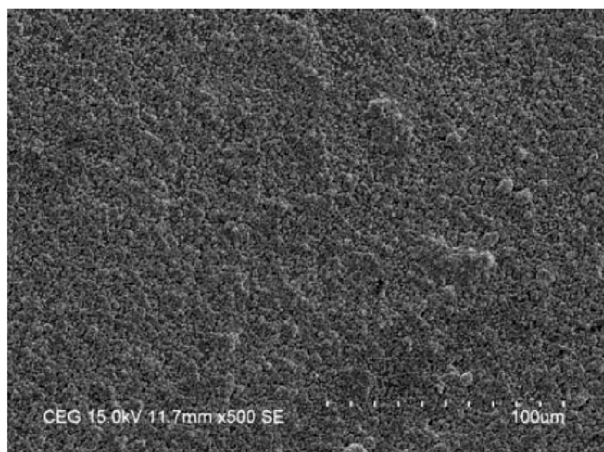


Fig. 15a. SEM photograph of electrolessly deposited copper with 1,2,3-benzotriazole x500.

Scanning electron microscope (SEM analysis):

The SEM photographs of electroless copper deposited specimens for plain and additive baths are given in Figs. 11–15 at an enlargement of x500 and x1000. All the substrates reveal nodular growth of copper deposits. The deposits observed from copper methane sulphonate bath contained smaller grain size when compared with traditional copper sulphate-EDTA bath[46]. The SEM figures show fine grained structure of copper deposit. The surfaces were smooth with a grain size of less than 20 μm.

Conclusion

Conductive pure copper can be deposited by electroless technique from a green eco-friendly copper methane sulphonate bath after controlling the operative conditions and by adding suitable additives. The additives like 2MBT, imidazole, 1,2,4-triazole and benzotriazole increases the stability of bath with bright and quality deposits and also the morphology is good with fine grain size. Among these 2MBT shows good bath stability with low plating rate. The additives improve the colour and the quality of the deposits.

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