International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.1, pp 237-245, Jan-Mar 2013

Formulation Of Novel Electroless Plating Process For Cu And Cu-P Alloys

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Abstract : A new electroless plating formulation has been optimized based on copper sulphate, formaldehyde and sodium hypophosphite with addition of EDTA+TEA .The new bath was found stable and operated upto 2 hours. It was found that the incorporation of phosphorus in copper matrix increased the corrosion resistance of the coatings both in as plated and annealed condition. The characterization of copper and copper-Phosphorus coatings were carried out by weight gain, Vicker's hardness , potentiodynamic polarization and impedance analysis. The surface morphology of the coatings were analyzed by XRD and SEM.

Keywords: Novel Electroless Plating Process, Cu And Cu-P Alloys.

Introduction:

Electroless plating is the process of deposition of metals with help of reducing agents. The process dates back to the first work by Brenner and Riedel. The general American transportation Corporation (G.A.T.C) adapted the process developed by Brenner and Ridell to coat interior of tankers that carry concentrated caustic soda and the process was called as "Kanigen process". In this type of plating, the deposit itself acts as its own catalyst and the plating proceeds as long as the work piece is immersed in the electroless solution. Electroless nickel plating; electroless copper plating etc. are some examples for this of plating.

When a properly cleaned and activated material is introduced into the electroless plating solution, the cations in the solution organize themselves into a blanket called matrix. The matrix covers the surface and controls the deposition process. The reducing agents in the solution get oxidised to release electrons at the interface. By several sequential reactions within the matrix, the metal ions in solution are reduced forming the coating. To sustain the reduction reactions, additions of fresh chemicals must be made. In addition to this, the concentrations of the special addition agents that influence the brightness, wetting and stability must be monitored and kept at optimum levels. Copper is a ductile metal, and pure copper is soft, malleable, nonmagnetic and non-sparking, whereas steel is magnetic, and some of its forms can be manipulated to make a variety of shapes and forms. Copper is a constituent of various metal alloys, and steel is itself an alloy. Common usage of copper is in military applications, weaponry, electrical wiring, plumbing and heating applications, piping, cooking utensils and for coinage [1-9]. The copper in solution is reduced onto the surface of the substrate by the following reaction (involvingformaldehyde as the reducing agent):

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

For deposition to occur, the redox potential of the reducing agent has to be more negative than that for the metal being deposited. The redox potential for the oxidation half reaction becomes more negative when the pH of the electroless deposition solution is increased. In an electroless copper deposition process with formaldehyde as the reducing agent, only an alkaline electrolyte can be used. Besides formaldehyde, hypophosphite [l0, 11], borohydride [17,] hydrazine [14], dimethylamine borane (DMAB) [18,] glyoxylic acid [19] and redox-pairs [14] (i.e. Fe(II)/Fe(III), Ti(III)/Ti(IIII), Cr(II)/Cr(III), V(II)/V(III)) have been investigated as reducing agents in electroless copper deposition solutions. Formaldehyde [2,20], DMAB [13,] hypophosphite [l0] and glyoxylic acid [19] have also been investigated as candidates for reducing agents in electroless copper deposition processes for very large scale integration (VLSI) applications**.** The aim of this work is to investigate the effects of incorporation of Phosphorus particles and the Phosphorus concentration on the anticorrosion properties of Cu–P and Cu coatings by using high stable bath on carbon steel substrates in 3.5% NaCl solution by using potentiodynamic polarisation and EIS techniques.

Karthikeyan etal [23]and Liang etal [24] have reported a copper sulpahte, $H_2PO_2^-$,EDTA (Complexing agent) and glyoxylic acid (reducing agent) based electroless copper bath. But bath stability is reported to be confined to the pH range 4 – 4.5. In the present investigation it is aimed to develop the same hypophosphite, based bath with wider pH range of operation (12.5), stability and sufficient the plating rate.

Experimental methods :

The bath used in the present study had the following composition:

Copper Sulphate ($CuSO_4$) - 6 gm/L
Ethylenediaminetetraacetic acid (EDTA) - 40 gm/L
Formaldehyde (CH_2O) - 8 ml/L
Sodium Hydroxide (NaOH) - 6 gm/L
Triethanolamine - 10 ml/L
Benzylidene acetone (Brightner) - 0.4 ml/ L
N-ethyl perfluoro-octane-sulfonamide (Surfactant) -2 ml/ L

The bath is maintained at 60°C.

For cu-P,coatings, sodium hypophosphite was added from 2-12 gl^{-1} , and 10 gl^{-1} was found as optimum concentration for coatings with enhanced mechanical properties.

Evaluation of the coatings through different techniques

Weight –gain method

For evaluation of plating rate the weight gain experiments were performed. Specimens of size 2 x 5 x 0.2cm,mild steel were used as the substrate. The steel panels were activated in dilute HCl bath and their initial weights were noted. Over them Electroless copper was carried out. In most cases the initiation was complete with in 25sec. A hole was punched near the top of the specimens to suspend then them into the plating solution. The bath pH and temperature were maintained to the desired level. No agitation was provided during the plating and the experiment was carried out for an hour. After the period, the specimens were removed, washed, rinsed with distilled water, dried and then re-weighed.

Rate of deposition (μ/hr) =

$$\frac{\mathbf{W}\ \mathbf{x}\ 60\text{x}10000}{DAt}$$

Where W = weight of the deposit (g)
D = density of the deposit **;**
t = plating duration (min);A = surface area of the specimen (cm^{-2})

Hardness measurements for all the as plated specimens and also for the heat treated samples at 400^o C were made by Vicker's hardness tester with a load of 100 g.

The polarisation studies were carried out using $1cm^2$ area of electrolessly copper coated specimens as the working electrodes. The measurement was made with BAS –100A, Electrochemical analyser. The polarisation cell has a three electrode cell assembly. The auxiliary electrode and the reference electrode used were of platinum plate of $4cm^2$ area and saturated calomel electrode respectively. A constant quantity of 200ml of 3.5% NaCl solution was taken in a 250ml beaker. The working electrode, reference electrode and the auxiliary Platinum electrodes were assembled in position and the connections were made. The bath temperature and pH were maintained at 65±1°C and 5.5±0.1°C. No agitation was provided. The scan rate was 10 mV/sec**.** The EG&G Princeton Applied Research – Model 6310 impedance analyzer was used for this measurement. The real part (Z') and the imaginary part (Z'') of the cell impedance were measured for various frequencies (100 kHz to 10mHZ) using the frequency response analyzer. The impedance measurements were carried out both the as plated and annealed electroless copper deposits. From the Nyquist plot, the charge transfer resistance and double layer capacitance values were calculated.

The X-ray diffraction patterns for the electrolessly deposited copper specimens were made both in the as plated as well as heat-treated (400^{o}C) conditions. These measurements help to explain the amorphous or the crystalline form of the deposits. The Electroless copper plated specimens with copper base were used for SEM studies. The photographs were portrayed at x 1000 with deposits in the as plated as well as heat treated conditions for Ni-P deposits, to have an idea of the surface morphology. The principle of the estimation is based on precipitating phosphorus completely as ammonium phosphomolybdate, dissolving the precipitate in standard HNO_3 solution and the excess HNO_3 being estimated through back titration procedure using NaOH as titrant [23,26,27]. The copper is analysed through EDTA complexometric titration method.

Results and Discussion

Effect of copper sulphate

It is found that when the concentration of copper sulphate is increased the rate of deposition increases sharply, but beyond certain concentration, the rate of deposition starts decreasing. For concentration of 6 gl^{-1} and above, the bath becomes turbid due to the hydrolysis of Cu^{2+} ions. The results are presented in **table 1.** The optimum concentration of copper sulphate to give the maximum rate was found to be 6 gl^{-1} (0.01M).

Table 1. Effect of copper sulphate concentration on rate of deposition

Copper Sulphate (g l^{-1})	Rate of deposition (« hr^{-1})
1	9.5
2	10.4
3	11.0
4	13.2
5	14.8
6	16.2
7	Bath decomposed

Effect of sodium hypophosphite

Sodium hypophosphite is the reducing agent used in the present study and it is the source for phosphorous in the alloy. The dependence of the deposition rate on the concentration of sodium hypophosphite is **given in table 2. It** is noted from the table that increasing the concentration of sodium hypophosphite results in increase in the deposition rate. A plating rate of about 13 to 16 μ/hr is realized as the concentration of sodium hypophosphite is varied from 2 g/l to 12 g/l. At higher sodium hypophosphite concentration bath stability is decreased. Thus the optimum concentration of sodium hypophosphite is found to be 10 gl^{-1} (0.2M).

Table 2. Effect of sodium hypophosphite on rate of deposition

Sodium hypophosphite (in M)	Rate of deposition (« hr^{-1})
2	8.4
4	10.6
6	13.3
8	15.0
10	16.2
12	decomposed after 30 min.

Effect of complexing agent

In addition to copper ion and reducing agent, the bath must contain a complexing agent. The complexant is necessary to prevent the precipitation of the basic copper salts together with copper compounds of the reducing agent and their breakdown products.

Triethanlamine , a monobasic compound having much volatility than diethanoamine and mono ethanolamine is found to be capable of acting as a complexing agent effectively. Further more, it can also exert high stability when coupled with EDTA ,the latter is widely used complexing agent in electroless copper deposition. The variation of deposition rate with the concentration of Triethanol amine+EDTA is **shown in table 3.** When its concentration is 40g (EDTA)+ 20ml(TEA) the highest deposition rate is achieved.

Table 3 .Effect of complexing agent on rate of deposition

Concentration of EDTA + Triethanol amine (in g/l)	Rate of deposition (« hr^{-1})
40g + 2 ml	10.0
40g + 6 ml	10.8
40g + 10 ml	11.6
40g + 14 ml	13.2
40g + 18 ml	15.0
40g + 20 ml	15.9
40g + 22 ml	17.0

Effect of pH

The reduction of copper ions by hypophosphite during electroless copper plating is favoured at high pH. It is thus anticipated from the above stoichiometry, that the plating rate is to increase with the solution pH. The effect of pH's on the deposition rate is given in **table 4.** To plate at the highest rate, the favourable pH value is found to be 12 .5± 0.1. However above the pH value of 13, it is noted that the deposits are stressed which is evident from their tendency to brittleness.

Effect of temperature and plating time

The autocatalytic electroless deposition reactions are usually dependent on the temperature and plating time. The effect of temperature on the plating rate was studied and the results are presented in **table 5 (a), where the increase in the plating rate with temperature is ob**served. The bath stability decreases as the temperature increases. In order to obtain a practical compromise between the two opposing effects the practical operating temperature is fixed at 65± 1 ^{o}C.

Table 5 (b) gives the variation in the deposition rate with plating time. The initial plating rate was found to be high particularly, in the first half an hour compared to that in the latter stages. This could be due to the consumption of various ingredients in the bath. Therefore periodic replenishment should be made and also the adjustment of required pH value to keep up the optimum-plating rate.

Evaluation of Mechanical properties of coatings by different techniques

Weight gain studies

The results of electroless copper deposition rates obtained in the present study by weight gain method are presented in table 6.

Hardness

The hardness of the electroless Copper and Cu-P alloy deposites measured by Vicker's hardness tester both in the as plated as well as heat treated condition is given in **table 7.** The higher hardness of electroless Cu-P coatings after heat treatment is due to the formation of precipitation hardening mechanism of coatings. Similar observation has been made earlier by Karthikeyan et al for electroless nickel coatings[23,26-28].

Table 4 .Effect of pH on rate of deposition

PH	Rate of deposition («/hr)
4	7.6
6	8.1
8	8.8
10	13.2
12	**15.3**
> 13	Stressed deposits obtained

Table 5 (a). Effect of temperature on rate of deposition

Temperature (^{o}C)	Rate of deposition («/hr)
45	5.5
50	7.4
55	9.0
60	10.2
65	15.0
>65	Bath decomposed after 65 mins.

Table 5 (b) Effect of plating time on rate of deposition

Plating Time (minutes)	**Rate of deposition («/hr)**
30	20.0
60	15.0
90	11.8
120	8.6
150	3.5

Table .6. The Results of Weight Gain Studies

Deposit	Rate(µ)
Copper	15
Cu-P	15.6

Table 7. Hardness Measurements

Deposit	Hardness (V.H.N)
Copper	150
Cu-P	370

Potentiodynamic polarization measurements for corrosion resistance of coatings

The electrochemical results obtained from the polarization studies for the carbon steel, electroless copper and Cu–P coatings in aerated 3.5% sodium chloride are shown in Figure 1. The Copper and and Cu–Pcoatings show relatively good resistance to corrosion in 3.5% NaCl. The presence of phosphorus shifted the corrosion potential, E_{corr}, to the right and decreased the corrosion current density, I_{corr} and consequently improved the corrosion resistance. Comparison of the electrochemical parameters (Table 2) of the electroless Cu ,Cu–P composite coatings and carbonsteel reveal that E_{corr} shifted towards the more noble direction and I_{corr} values decreased with the incorporation of phosphorus particles in the electroless matrix, indicating a better corrosion protective ability of coatings both in the asplated as well as annealed condition.

Electrochemical impedance spectroscopy (EIS) studies

The measured impedance spectra of the carbon steel substrate, electroless Cu–P and Cu–P (annealed) coatings in 3.5% NaCl solution are shown as Nyquist plots in Figure.2. It is evident from Fig.4.2 that the formation of a single semicircle or a semicircle in the high frequency region followed by a low frequency loop is typical of metallic coatings [28,29]. Although the curves in the Nyquist plot appear to be similar with respect to their shape, they differ considerably in their sizes. This indicates that the same fundamental processes must be occurring on both the Cu–P and Cu–P (annealed) composite coatings but over a different effective area in each case. The semicircle at the high frequency region represents the coating response, while the loop at the low frequency region is associated with simultaneous physicochemical phenomena at the metal/coating/solution interface According to Contreras et al. [31] the loop at the lower frequency region is associated with the double layer capacitance and/or diffusion phenomena of the oxidant chemical species through the porous coating (for mild steel). The Rct and Cdl values increased and decreased, respectively, with the heat treatment of Cu–P composite coatings. The annealed electroless Cu–P has the highest values of Rct and lowest values of Cdl implying the better anti-corrosion ability. The Rct of annealed Cu–P and as plated Cu– P coatings are 2440 and 1054 µF cm^{-2}, respectively, and the corresponding Cdl values are 1.48 µF cm^{-2} and 9.86 µFcm^{-2} respectively.The Rct and Cdl values for electroless copper and mild steel are 1317 and 810 ,and the corresponding Cdl values are 7.71 µF cm^{-2} and 14.24 µF cm^{-2} .

Surface morphology of the electroless copper coatings

The results of XRD analysis, are shown in **Figure 3.** The crystalline peaks in figure are resulted from the Cu substrate. A broad peak appearing around 2Ø of 718 indicates that the deposits are amorphous. This is in correspondence with the knowledge that an electroless copper deposit would become amorphous when its P% is above 7 wt.% [23,28-30].The peaks at 97 and 110 correspond to the existence of P in electroless copper with phase formation of Cu_3P through precipitation hardening mechanism .The formation of Cu_3P is achieved by annealing the coatings at 400ºC, which accounts for the highest hardness of electroless Cu-P coatings than copper.

Scanning Electron Microscopic studies

It can be found that the morphology changes remarkably. For the optimum samples (Cu-P), the best evenness and compactness can be observed and needle holes hardly appear on its surface from SEM images as shown in figure 4 (b).. For the samples without phosphorus, not only a large number of layered holes appear on microstructure surface, but also the evenness and compactness get worse as shown in Figure 4 (a).

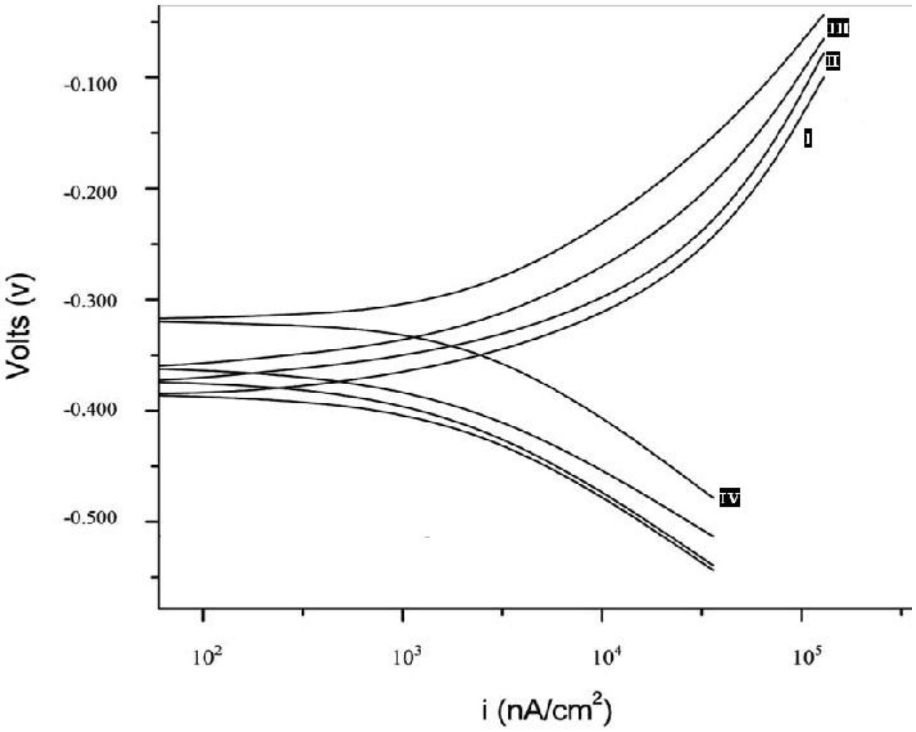

Figure 1.Potentiodynamic polarization studies of electroless Cu-P deposits: Electrolyte: 3.5 %NaCl.

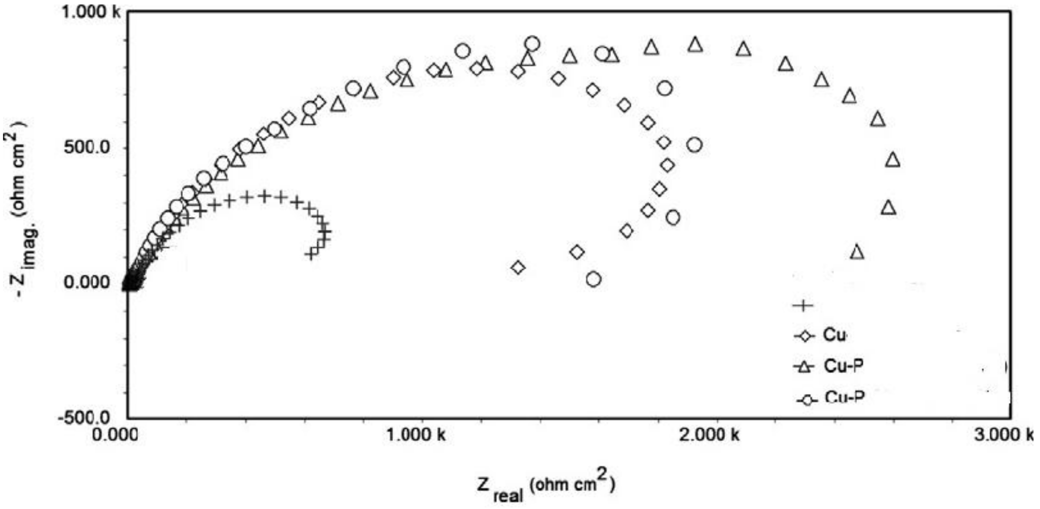

Figure 2 .Impedance studies of electroless Cu-P deposits:Electrolyte: 3.5 %NaCl.

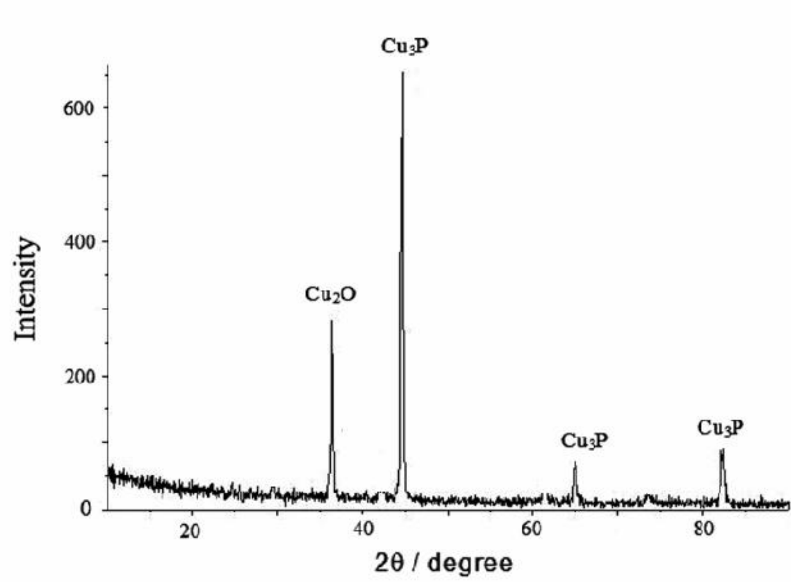

Figure 3.XRD analysis of Electroless Cu-P coatings (Annealed)

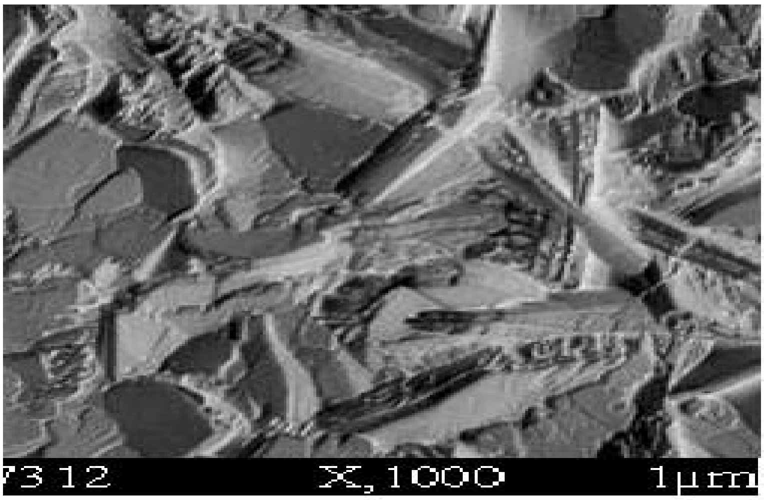

Figure 4 (a) SEM for electroless copper deposit.

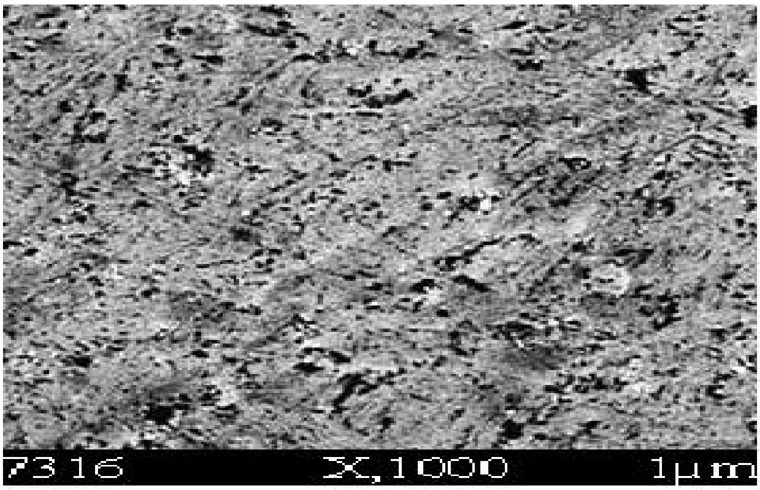

Figure .4 (b) .SEM for electroless copper –phosphorus deposit

Conclusion

1. A suitable bath has been formulated based on copper sulphate,hypophosphite and mixer of EDTA+ Triethanol amine to get electroless copper and Cu-P alloy.
2. The incorporation of phosphorus into Copper matrix enhances the corrosion resistance of the coatings.
3. The high hardness of electroless Cu-P is due to the formations of Cu_3P by Precipitation hardening Mechanism.
4. The better performance of Corrosion Resistance of Cu-P then Mild Steel is achieved both in the as plated and annealed condition.
5. The potentio-dynamic polarization studies for electroless Cu-P shifts E_{corr} and I_{corr} to the positive direction confirms the superior performance for Cu-P deposits.
6. The increased Rct and decreased Cdl values for electroless Cu-P indicates that the coating offers resistance to corrosion.
7. The existence of Cu_3P is confirmed by X-Ray Diffraction studies.
8. The SEM studies confirm the presence of Phosphorous in Copper matrix through the formation of compact and even surface.

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