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EFFECT OF ADDITIVES ON STRUCTURE AND PROPERTIES OF ELECTRODEPOSITED NANOCRYSTALLINE COPPER

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ABSTRACT

The effect of additives, thiourea and gelatine on the electrodeposited nanocrystalline copper using acid copper sulphate electrolyte with optimized bath composition and process conditions was examined and the results were presented in this article. The XRD result shows that the average crystallite size calculated for the electrodeposited copper was ~14nm and for the copper with gelatine and thiourea additives was ~5.3nm and ~6.6nm respectively. The crystallite structure of the nanocrystalline copper with additives and additive-free deposits were crystalline fcc. The microhardness of the electrodeposits with additives enormously increased (~80%) compared to additive-free electrodeposits. This improved microhardness is due to the reduced grain size of the electrodeposits. The measured cathode current efficiency (CCE) and throwing power (% TP) of the electrodeposition bath has been found to increase by the addition of additives compared to additive-free electrodeposition. The SEM micrograph shows the smooth, pore-free and fine-grained electrodeposits with additives compared to additive-free electrodeposition.

Keywords: Electrodeposition, Nanocrystalline Copper, Additives, Gelatine, Thiourea, Microhardness.

INTRODUCTION

In recent years, nanostructured materials have shown considerable interest due to their improved mechanical, physical, chemical, electrical and electrochemical properties. Different methods are used for the production of nanostructured materials. Among the various methods available for the production of nanostructured materials, the simple, low cost direct current electrodeposition method is one of the excellent techniques used for the synthesis of nanomaterials. The dense, uniform and fine-grained deposits were obtained by passing a direct current through the electrolysis cell. The coating obtained by the electrodeposition method was used for decorative and protective purposes and to enhance the specific properties of the metal surfaces. One of the first applications was the electrodeposition of copper on printing press plates. Then afterwards, the electrodeposition of copper is utilized in numerous engineering and decorative applications. Presently, the electrodeposited materials are widely used for many industries, such as automobile, electrical and electronics, jewellery, ship, aerospace, machinery, defense, and toy industries etc.[1,2]

The major factors, which affect the structure and mechanical properties of the electrodeposited coatings are; bath composition, bath agitation, temperature and pH of the bath and the use of additives. Among the different parameters, the use of additives, which affect the grain size and surface roughness and also the mechanical properties of the coatings. The organic (or) inorganic compounds, which are used in the electroplating bath as additives to get pore-free, smooth and bright electrodeposits[3-7]. In copper electrodeposition, the various additives, so far endeavored to better the physical and mechanical properties of the electrodeposits are; Thiourea, Gelatine, Chloride anions, polyethyleneglycol, ethylenediamine, dodecyltrimethylammonium chloride (DTAC) and bis(3-sulphopropyl) disulphide (SPS), benzotriazole etc.[8-20] Some of the recent literature reported that, additives play a major role in the improvement of the surface properties of the electrodeposited metals to a larger extent.[21-30] The scope of the present work is to find out the effect of two additives, gelatine and thiourea on the electrodeposition of copper from acid copper sulphate electrolytes.

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EXPERIMENTAL

Electrodeposition of Nanocrystalline Copper

Thin copper films were prepared by electrodeposition technique using an acidic $CuSO_4$ bath as the electrolyte. The chemicals used in the electrodeposition process have been purchased from Merck. Electrodeposition was carried out using the copper bar of the high pure anode (99.95%) and mechanically polished, degreased and chemically cleaned stainless steel plate of 2×2 cm^2 area was used as the cathode material. The electrolyte composition was $CuSO_4.5H_2O$ (225 g/L) and H_2SO_4 (70 g/L). Thiourea and gelatine are used as additives in the electrodeposition bath and their concentrations are 20 & 50 mg/L respectively. The optimized current density was 2 A/dm^2. The electrodeposition bath temperature was maintained at 30ºC and the pH of the bath was maintained at ~1. The deposition time was taken for 60 minutes per deposit (Table-1). The copper thin film with a thickness of approximately 80µm was electrodeposited on a stainless steel substrate. The additive-free copper electrodeposits were also obtained with the same processing conditions for the comparative study. After the deposition, the electrodeposited samples were cleaned and dried and used for different characterization studies.

Table-1: Electrodeposition Bath Composition and Conditions

Electrodeposition Bath Constituents	Bath Concentrations (Bath-1)	Bath Concentrations (Bath-2)
Copper sulphate ($CuSO_4.5\ H_2O$)	225 g/L	225 g/L
Sulphuric Acid (H_2SO_4)	70 g/L	70 g/L
Thiourea	20 & 50 mg/L	-------
Gelatine	-----	20 & 50 mg/L
Current density	2 A/dm^2	2 A/dm^2
pH	~1	~1
Temperature	30˚C	30˚C
Time	60 min	60 min

Throwing Power and Cathode current efficiency

Throwing power is a measure of how evenly a metal is deposited over the surface from the high to low current density areas. Haring and Blum Cell was used to find out the throwing power of the electroplating bath. This is a long narrow plating box made of PVC with one anode and two cathodes are placed at a relative distance of 12.5cm and 2.5cm from the anode (i.e. 5:1 ratio). For calculating the throwing power percentage, Field's formula is used.

$$\% \text{ TP} = \frac{(L-M)}{(L+M)-2} \text{ X } 100$$

Where, L = Distance ratio i.e., the ratio of the distance between far cathode and near cathode from the anode and M = Metal ratio i.e., the ratio of the metal deposited on the near cathode and the far cathode. The cathode current efficiency of the electrodeposited copper with additive and additive-free electrodeposits is also measured based on the calculations of Faraday's laws of electrolysis.

Characterization of Electrodeposited Nanocrystalline Copper

The electrodeposited nanocrystalline copper with additives and additive-free samples are subjected to the following structural and morphological studies. The Vickers microhardness tester (Everyone microhardness analyzer) was used to measure the microhardness of the electrodeposited samples. The XRD (Bruker D8 Advance) analysis was used to measure the crystallite size and crystallite structure of the electrodeposited copper coatings using the Debye-Sherrer formula,

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

Where 'D' is the crystallite size, 'β' is the FWHM (full width half maximum height) of the peak and 'λ' is the wavelength of radiation. The surface morphology of the electrodeposited coatings to be analyzed by SEM (Hitachi, Japan Model; S3000H) studies.

RESULTS AND DISCUSSION

Throwing Power (%TP) and Cathode Current Efficiency

The throwing power was determined with additives thiourea and gelatine and additive-free copper electrodeposition at the current density of 2 A/dm^2 with DC current and the results are shown in Table-2. The throwing power of the electroplating bath with additives, gelatine and thiourea was found to increase compared to additive-free electrodeposition. It is observed that, the presence of additives increases the throwing power, also enhances the uniform deposition and grain growth (Table-2).

The cathode current efficiency of the acid copper sulphate electroplating bath with gelatine and thiourea additives and additive-free electrodeposition was measured by Faraday's laws of electrolysis. It is observed that, the cathode current efficiency of the bath was found to increase in the presence of additives compared to additive-free electrodeposition. This infers that the current passed through the electrolysis cell is completely utilized for the reduction of copper on to the cathode surface.

Table-2: Throwing Power Efficiency of the Copper Electrodeposition Bath.

Nature of Sample	% Throwing Power
Electrodeposited copper (additive free)	26
Electrodeposited copper with 20 mg/L gelatine additive	28
Electrodeposited copper with 50 mg/L gelatine additive	31
Electrodeposited copper with 20 mg/L thiourea additive	27
Electrodeposited copper with 50 mg/L thiourea additive	29

Effect of Additives on Microhardness of Electrodeposits

The Vickers microhardness was assessed for the cleaned electrodeposited copper samples utilizing an Everyone microhardness analyzer with a load of 10g and a stay time of 5s. The measured Vickers microhardness of electrodeposited copper samples as a function of the concentration of gelatine and thiourea is shown in Table-3. The microhardness of the electrodeposited nanocrystalline copper with additives gelatine and thiourea were increased (~80%) compared with the additive-free copper electrodeposit. This increase in microhardness is because of the grain refinement, i.e. the grain size tends to lessen with an increase in the concentration of additives. The additives act as a grain purifier since the added substances, for example, gelatine and thiourea impede the deposition of copper from sulphate bath and enrich the nucleation process and produce nanocrystalline copper with an average grain size of below ~10nm. Accordingly, the improved friction and wear properties were also expected from the electrodeposited nanocrystalline copper.

Table-3: Vickers Microhardness of Electrodeposited Nanocrystalline Copper

Electrodeposited Samples	Vickers Microhardness (HV) in Kg/mm^2
Electrodeposited copper	65
Electrodeposited copper with 20 mg/L gelatine	88
Electrodeposited copper with 50 mg/L gelatine	117
Electrodeposited copper with 20 mg/L thiourea	85
Electrodeposited copper with 50 mg/L thiourea	115

Effect of Additives on the Crystallite Size and Crystallite Structure of the Electrodeposits by XRD Analysis

Electrodeposited Copper with 20 and 50 mg/L of Gelatine Additive

The crystallite size and crystallite structure of the electrodeposited copper coatings with gelatine additives and additive-free electrodeposits were assessed by XRD analysis and the results are shown in Table-4 (Fig.-1). The crystallite size was measured using Debye-Scherer's formula from XRD information was 14nm for electrodeposited nanocrystalline copper and 7.4nm and 5.3nm for electrodeposited nanocrystalline copper with 20 and 50 mg/L of gelatine additives respectively. The crystallite structure was crystalline fcc for the electrodeposited nanocrystalline copper with the high intense peak of (111). The additional peaks with 2θ values of 16.72, 32.50, 36.71 and 39.89 are confirming the presence of gelatine on copper and this makes the deposit smoother and brighter, even though the structure of the

electrodeposits were not much deviated from crystalline fcc, which was matched and confirmed from the JCPDS standards (Fig.-1).

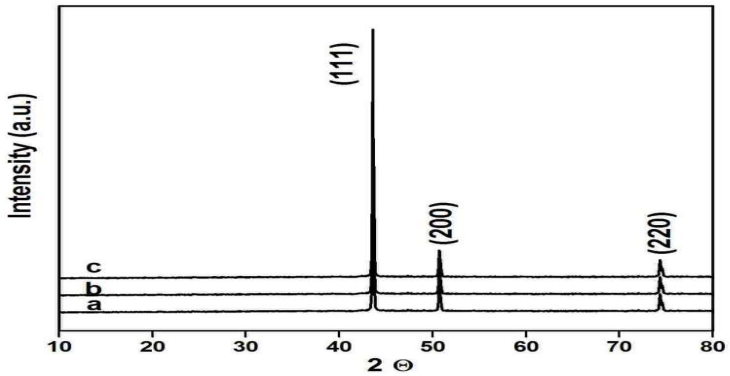


Fig.-1: XRD Patterns of Electrodeposited Copper, (a) Additive-free (b) with Additive 20 mg/L of Gelatine, (c) with Additive 50 mg/L of Gelatine

Table-4: Parameters Derived From XRD Pattern of Nanocrystalline Copper with Gelatine Additive.

Electrodeposit Details	2θ	d-spacing (A°)		Miller Indices (h k l)	Lattice Parameter		Str./ Phase	Average. Cryst.Size. (nm)
		Observed (A°)	Standard (A°)		Observed	Standard		
Additive-free Copper	43.5801	2.07512	2.0883	(111)	a = 3.600	a=3.615	fcc	~14
	50.6961	1.79928	1.8082	(200)				
	74.3416	1.27492	1.2780	(220)				
Copper with 20 mg/L of Gelatine	43.6419	2.07233	-	(111)	a=3.596	a=3.615	fcc	~7.4
	50.7543	1.79735	-	(200)				
	74.4037	1.27401	-	(220)				
Copper with 50 mg/L of Gelatine	43.5834	2.0749	-	(111)	a=3.599	a=3.615	fcc	~5.3
	50.7030	1.7990	-	(200)				
	74.3656	1.2746	-	(220)				

Electrodeposited Copper with 20 and 50 mg/L of Thiourea Additive

The crystallite size and structure of the electrodeposited copper coatings with thiourea additive and additive-free samples were assessed by XRD analysis and the results are shown in Table-5 (Fig.- 2).

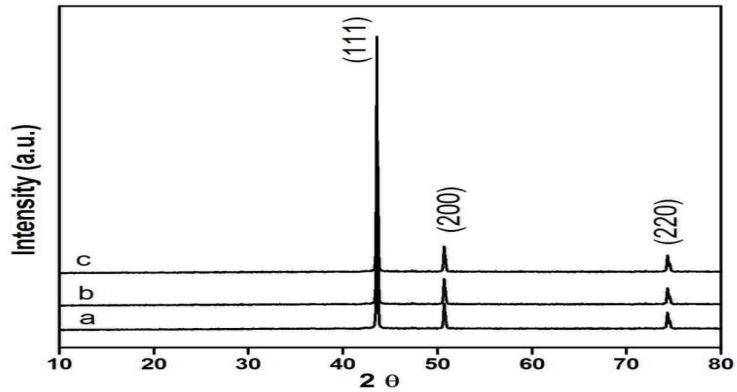


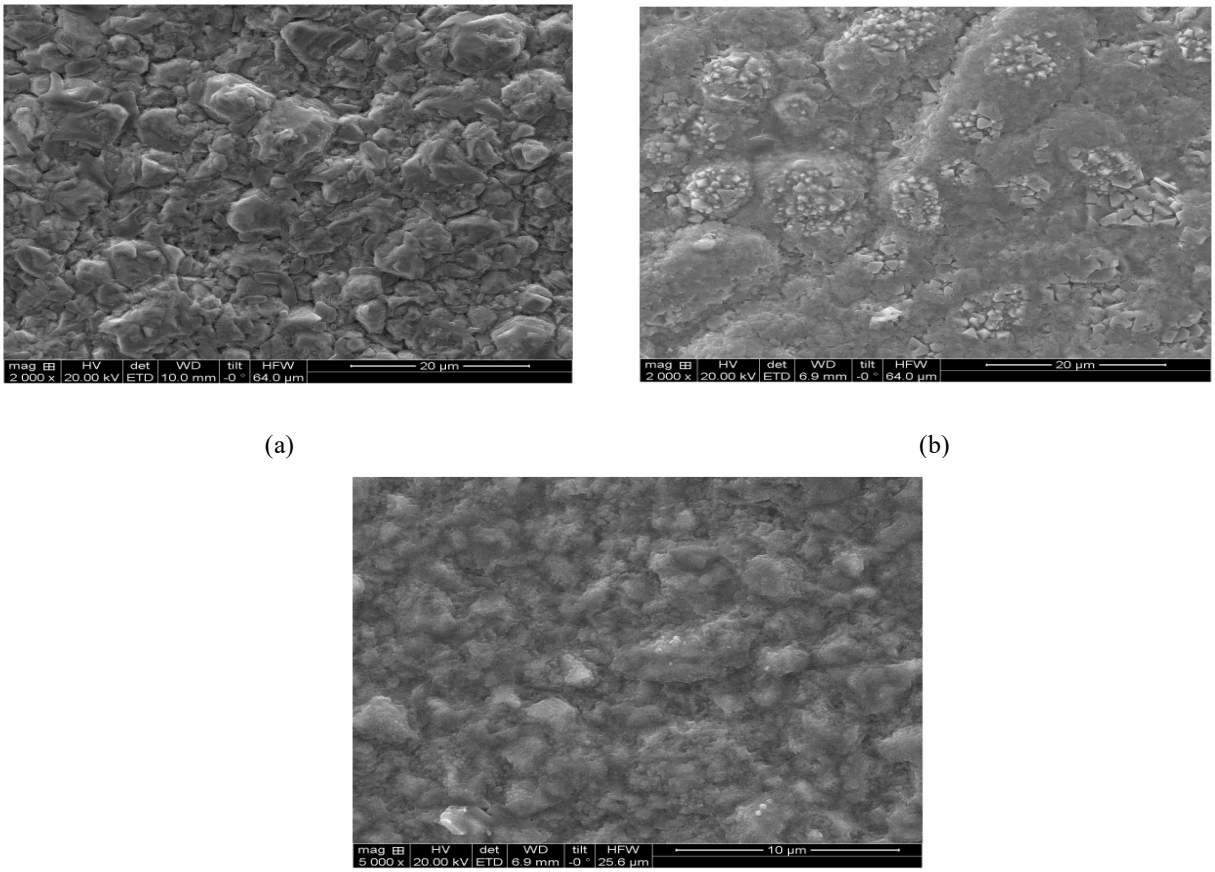
Fig.-2: XRD Patterns of Electrodeposited Copper, (a) Additive-free,(b) with Additive (20 mg/L of Thiourea), (c) with Additive (50 mg/L of Thiourea).

The crystallite size determined (using Debye-Scherrer's equation) from XRD information was 14nm for electrodeposited nanocrystalline copper and 9.1nm and 6.6nm for electrodeposited nanocrystalline copper with 20 mg/L and 50 mg/L of thiourea additives and the structure was crystalline fcc for the

electrodeposited nanocrystalline copper with the high intense peak of (111) was obtained. The additional peaks with 2θ values of 16.71, 24.22, 25.07, 29.83, 33.71, 36.70, 39.23, 42.55, 61.65 & 66.11 are confirming the presence of thiourea on copper; also this makes the electrodeposits smoother and brighter (Fig.-2). From the results, it is observed that the average crystallite size was measured for electrodeposited copper is 14nm and for electrodeposited copper with 50 mg/L thiourea additive is 6.6 nm. This reduced crystallite size of the electrodeposits shows increased microhardness and possible other mechanical properties.

SEM Analysis

The SEM images of the electrodeposited nanocrystalline copper with additives and additive-free electrodeposits are shown in Fig.-3(a, b, c). The surface morphology of the electrodeposits with additives shows brighter and smoother surface and uniform crystal growth compared to additive-free electrodeposits (Fig.-3b, c). The additive-free electrodeposits show dull and rough surface appearance compared to electrodeposited copper with additives (Fig.-3a).



(a) (b)

(c)

Fig.-3: SEM Micrograph of (a) Electrodeposited Copper (additive free), (b) Electrodeposited Copper with 50 mg/L Thiourea, (c) Electrodeposited Copper with 50 mg/L Gelatine.

Table-5: Parameters derived from XRD pattern of Nanocrystalline copper with thiourea Additive.

Electrodeposit Details	2θ	d-spacing (A°)		Miller Indices (h k l)	Lattice Parameter		Str./ Phase	Average. Cryst.Size. (nm)
		Observed (A°)	Standard (A°)		Observed	Standard		
Additive free Copper	43.5801	2.07512	2.0883	(111)	a = 3.600	a=3.615	fcc	~14
	50.6961	1.79928	1.8082	(200)				
	74.3416	1.27492	1.2780	(220)				

Copper with 20 mg/L thiourea	43.5254	2.0776	-	(111)	a=3.602	a=3.615	fcc	~9.1
	50.6623	1.8004	-	(200)				
	74.2999	1.2755	-	(220)				
Copper with 50 mg/L thiourea	43.5871	2.0748	-	(111)	a=3.598	a=3.615	fcc	~6.6
	50.7085	1.7984	-	(200)				
	74.4544	1.2733	-	(220)				

CONCLUSION

The nanocrystalline copper thin film was successfully prepared by electrodeposition technique with gelatine and thiourea additives. From the XRD results, the average crystallite size calculated was 14nm for additive-free copper and 5.3nm and 6.6nm for electrodeposited copper with gelatine and thiourea additives. The crystallite structure was crystalline fcc for the electrodeposited copper with additives and additive-free samples. The scanning electron microscopy (SEM) result shows that the electrodeposits were smoother and brighter for the electrodeposited copper with additives compared with additive-free electrodeposited samples. The cathode current efficiency and throwing power (% TP) of the electrodeposition bath has been found to increase by the addition of additives compared with additive-free electrodeposition. The electrodeposits with additives showed increased microhardness and reduced crystallite size than the additive-free electrodeposited copper.

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