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Thin film electrodeposition of nanostructured copper in presence of ultrasound

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Abstract

Electrodeposition of copper thin films of the order 4 μm was carried out potentiostaticly on metallic substrates with and without the presences of ultrasound. A simple acidic solution without any additives served the medium of deposits.Crystallinity and other details of average domain size and strain were carefully analyzed by X-ray diffraction (XRD) studies.Comparision of the line plots gives the highly crystallinity nature of copper deposits in presences of ultrasound and an amorphous impression for silent deposits. Domain size calculation gives a value of around 0.3μm in both the condition. The morphology of these copper deposits were systematically compared by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) methods respectively. The average grain size of Cu deposit was found in well agreement with the XRD results. A characteristic corncob like structure appears in silent Cu deposits where as the sonicated deposit is a compact one. Compositional study by EDS confers the impurity free deposit in ultrasound in terms of sulpher content and oxidation level.Resistivity measurement by four probe method further complies the EDS results.

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Introduction

Nanostuctured particles have attracted extensive scientific and industrial interest due to their unique electronic, optical, and catalytic properties[1,2].Copper is one of the metals most extensively used in industry, either because of its intrinsic properties or as a base to further formation of metallic films. Copper (Cu) thin films are used for various applications particularly for the preparation of ternary I–III–VI$_2$ semiconductors and fabrication of interconnections in semiconductor industry [3]. Among the various deposition techniques available for the preparation of Cu thin films, method of electrodeposition is an attractive technique because of its simplicity, low cost and possibility of making large area thin films [4, 5]. Sonoelectrochemistry is the study of the effects of the combination of ultrasonic radiation with electrode processes occurring at surfaces of electrodes immersed in a solution in an electrochemical cell. The ultrasound plays an important role to produce cavitation bubbles inside the electrolyte by rupturing the chemical bonds between molecules and electrolyte. The cavitation bubbles implosively collapse within a very short time after undergoing the formation growth and contraction. Collapsing a bubble generates higher temperature than the surrounding and results negative temperature gradient. Higher the negative temperature gradient, smaller the nuclei formed [6, 7]. In this process, metal nuclei are dissolved and deposited on the electrode during electrolysis of electrolyte where as a cavitation effect of ultrasound enhance the nucleation rates of the metal nuclei. This method is used to enhance the reaction rate in electrochemical process and produce the nanostructured thin films [8]. In recent years, electrochemical aspects of the electrodeposited Cu thin films prepared using potentiostatic conditions and physical properties of deposited Cu thin films have been reported by several authors. It has been revealed that the growth conditions affected the physical properties of the films. In this investigation nanostructured copper thin film are produced by electrodeposition technique with the application of ultrasound. These nanostructured thin films were characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM), EDS measurement and fourprobe method in order to study crystallinity and average domain size and strain, structural morphology, compositional analysis and electrical properties like resistivity of the films.

Experimental

Electrodeposition is used as a route to prepare nanostructured copper thin films. Prior to film deposition, aluminium substrates were cleaned with distilled water. Electrodeposition of nanostructured Cu thin films on aluminum substrates was accomplished in a three-electrode electrochemical cell containing electrolytic solutions of $CuSO_4$ (Cu = 10g/l), H_2SO_4 (100g/l) and rest distilled water. The counter electrode was a copper plate and saturated calomel electrode was used as the reference electrode. The electrolytic solution was taken in a glass jar and put it on an ultrasonic vibrator of frequency 20 KHz. The deposition was carried out in potentiostatic mode and at room temperature. The potential range applied for the deposition varied between +0.3V to +0.6V with reference to SCE at a scanning rate of 1mV/s. Before each scan and subsequent experiments, the electrodes were polished and rinsed with distilled water and dried. The dissolution of copper plate and deposition on aluminum plate has taken place in the working potential range. During electrodeposition the electrolytic solution was not stirred. The experiment was carried out both in silent and ultrasonic condition. After the sample has prepared it is characterized by XRD, SEM.

Results and Discussion

XRD analysis of both the sample silent and ultrasonic condition are shown in figure-1 .This pattern shows that the peaks corresponds to the copper peaks which are cubic in structure. The XRD plot shows that in silent condition more peaks are observed and the base line are hazy like structure which indicates the deposits are in powder form. Grain size from the Willamson-Hall formula gives a figure of around 360nm.

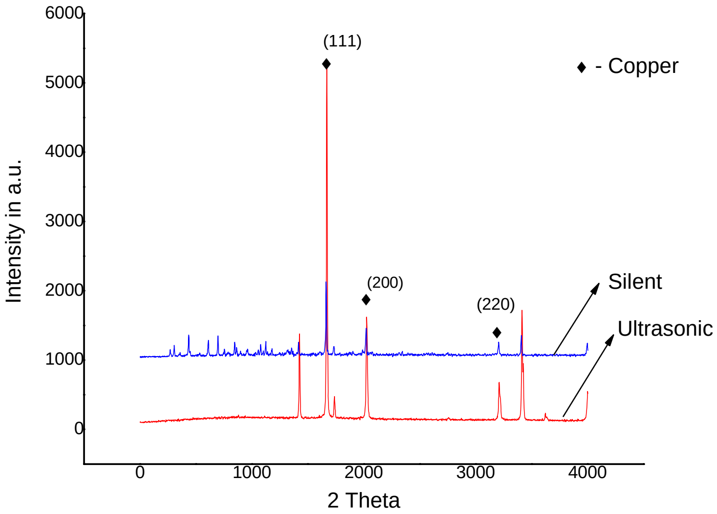
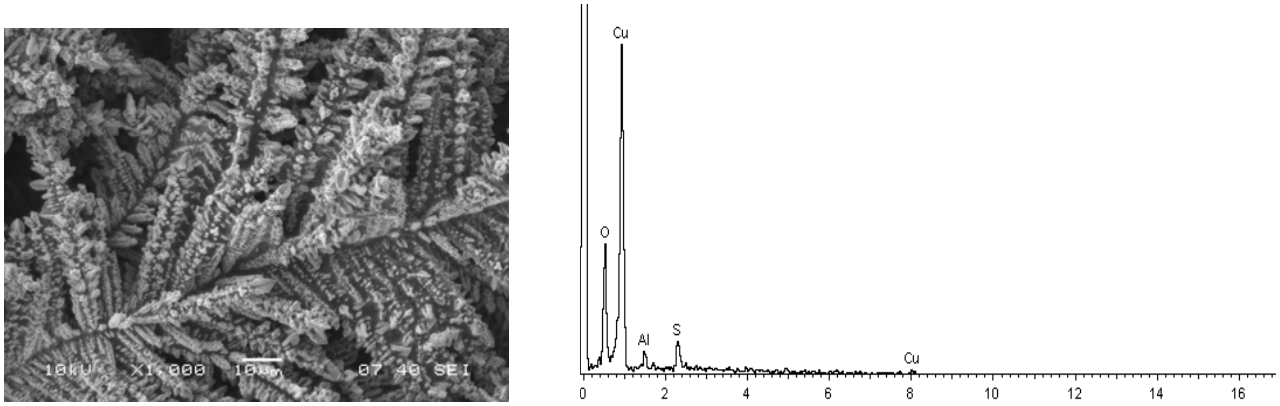


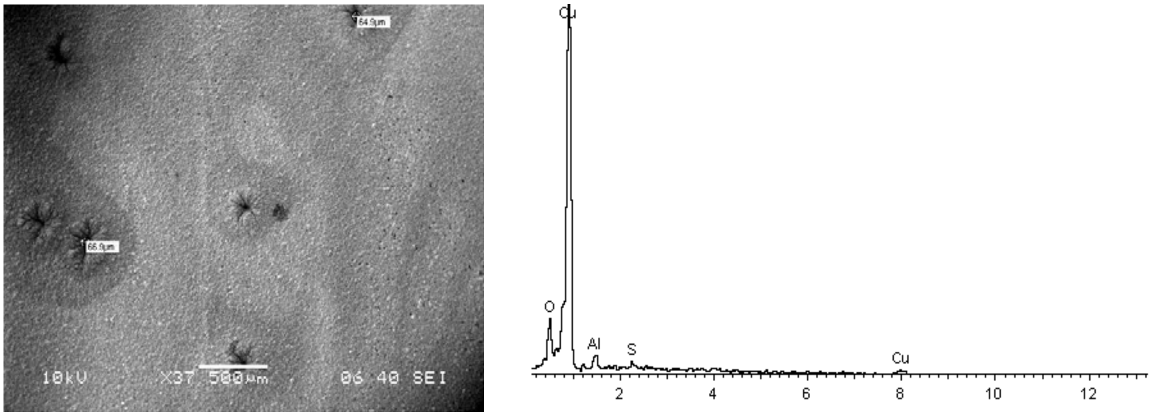
Fig-1.XRD plot of the copper deposits at ultrasonic and silent condition



(a) (b)

Fig. 2. (a) SEM image of silent copper deposit (b) corresponding EDS curve

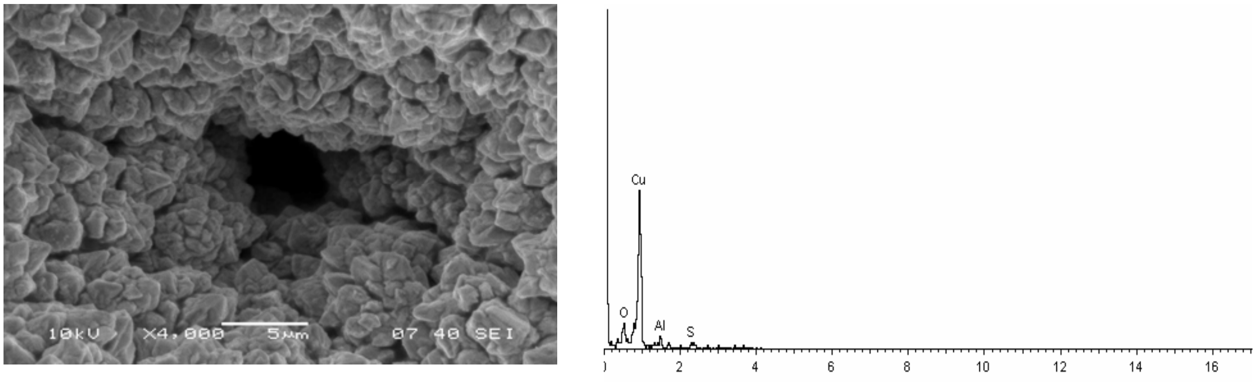
The figure-2 shows that the SEM microstructure of thin film copper deposits on aluminum substrate at room temperature both silent and ultrasonic conditions. Figure 2(a) shows that the copper deposits under silent conditions looks like dendritic structure or corncob structure. The corresponding plot of EDS confirms the copper phase along with some sulphur and oxygen, aluminium peak is due to the substrate material. On fig. 3 we have shown the deposit at very low magnification to confirm the microstream jetting effect of ultrasound.



(a) (b)

Fig. 3. (a) SEM image of ultrasonic copper deposit (b) corresponding EDS curve

The inward push of material indicates that the pores might be due to the above mentioned effect and not the evolution of any gases like hydrogen from the electrode. A magnified image of the same has been given in figure 4. The structure differ those from silent condition. Deposited domains look like mushroom configuration. This may be an indication of deposition in energy favorable direction which is far from conclusion.



(a) (b)

Fig. 4. (a) SEM image of ultrasonic copper deposit (b) corresponding EDS curve

Now comparing the percentage of oxidation and sulphur content form the EDS result, ultrasonically generated structures have low amount of oxygen and sulphur. This might be an indication that ultrasound forms the grains in low surface energy direction, so that the affinity for these interstitial elements is less, so complex formation tendency is less.

Conclusion

The characterization of copper thin films confirms the nanostructure which is prepared in this work. SEM micrograph concludes that the film prepared in ultrasonic condition is uniform, adherent and closely packed than in silent condition. XRD also reveals that copper is cubic in sructure and copper content is higher in ultrasonic prepared film with less content of impurities which is confirmed by EDS.

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