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Sonolectrochemically Deposited Nanostructured Copper Thin Films at Low Temperatures: Growth Kinetics and Nucleation Behaviour

A. Mallik and B.C. Ray

***Abstract*—Electrodeposition of copper are studied both in presence and absence of ultrasound at low temperatures (25°C, −2.5°C and −4°C). The deposits are analyzed and characterized by cyclic voltammetry (CV), chronoamperometry (CA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The diffusion coefficient along with the nuclei number density gradually increases under ultrasonic irradiation. The silent nucleation phenomenon has a transition from instantaneous to progressive nucleation in comparison to the instant appearance under insonation with decreasing temperature. Ultrasound also assists the secondary nucleation on the preexisting grains. The XRD analysis of the films confirms the copper crystallinity. XRD measurement along with the AFM analysis confirms the nano grains in the films. Good surface coverage and crystallinity under insonation can be observed from the SEM morphologies. The 3D topographical AFM analysis of the sonicated substrates further compliments the SEM analysis.**

***Index Terms*: Copper, Sonoelectrochemistry, Low-temperature, Nanostructure, Thin-Film.**

I. Introduction

In order to cater the need of enhanced reliability in electronics, copper thin films and lines have been emerged as a convenient alternative to aluminum in interconnections on printed circuit boards, systems in packages and semiconductor devices [1]. Electrochemical architecting of copper is one of the most convincing methods in fulfilling the film aspects towards adequate thickness, porosity-free structure and good adhesion. Technically supremacy of the method lies on the track of advantages of low processing temperatures, control of film thickness, and deposit onto complex shapes, low capital investment and the production of non-equilibrium materials that cannot be accessed by traditional processes [2]. Electrocrystalisation occurs either by the build-up of existing crystals or by the formation of new ones [3]. These two processes are in competition with each other and are influenced by the different operating parameters such as bath composition, pH, bath temperature, overpotential, bath additives. Low temperature supersaturates the phase and hence the final structure of the deposits [4]. Then again, ultrasonic irradiation further adds to the supersaturation event by the mechanism of cavitations and secondary nucleation [5,6]. Cavitation is the phenomenon of sequential formation and collapse of microscopic bubbles in the electrolyte. The two key mechanisms that have been identified as the measure of rate determining steps for ultra-fine crystal formation are charge transfer at the electrode surface and surface diffusion of adions on the crystal surface. For a supersaturated solution phase the former dominates the control of rate of the reaction whereas the reverse is true for a depleting ion concentration near an electrode. Thus, the effects have been experimented here with a copper system onto brass electrodes.

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II. Experimental Details

Electrochemical studies, of copper from sulfate solutions containing 0.1 M Copper and 60 g l^{-1} H_2SO_4, were conducted with a potentiostat/galvenostat (Eco Chemie Netherland, Autolab PGSTAT 12) system having computer interface of GPES software and three electrode system. Experiments were performed on O_2 free brass substrates of exposed surface area of 1×1 cm^2. A 5 cm platinum rod of 0.2 cm diameter and an Ag/AgCl electrode (Eco Chemie, Netherlands) served as counter and reference electrodes respectively. Before each scan and subsequent experiment, electrodes were polished, washed and dried properly. Ultrasound irradiation was accomplished by a 20 kHz ultrasonic horn with 20% output power transducer system (Sonics & Materials, VCF1500) fitted with a titanium tip. Low temperature electrodeposition and low temperature (25°C, −2.5°C and −4°C) sonoelectrodeposition studies were done with the electrochemical cell placed in refrigerator which temperature varies from room temperature to −20 °C. The temperature of electrolyte solution was measured with digital thermometer. The deposits were analyzed and characterized by cyclic voltammetry (CV), chronoamperometry (CA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM)

III. Results And Discussion

A. Cyclic Viltammetry

Cyclic voltammetry (CV) was performed in the [0.8 to –0.6] V potential range to identify the presence of the electrodeposition processes and to verify the electrochemical behavior of the electrodes in the elctrodeposition bath. Figure 1 shows typical CVs for brass electrodes obtained with a scan rate of 10 mV/s. Both voltammograms are characterized by the presence of cathodic-anodic peaks associated with deposition and dissolution of Cu. Furthermore, in the two curves, it is possible to note the presence of crossovers of the cathodic and anodic branches, typical of the formation of a new phase, involving a nucleation followed by diffusion limited growth process.

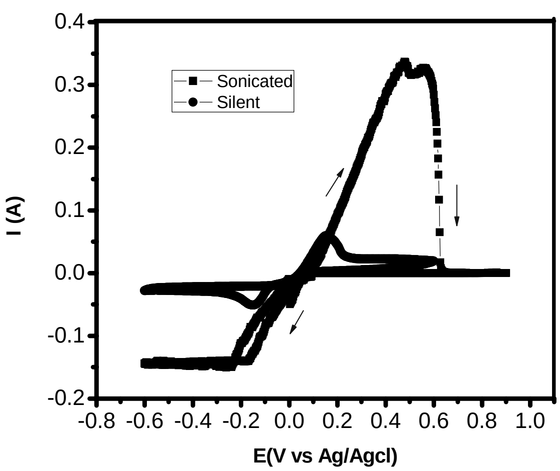

Fig. 1: Cyclic Voltammetry of Copper Deposition on Brass under Silent and Sonication at a Scan rat$e of 10 mV/s.

It is apparent from the figure that there is a significant increase in the amount of Cu deposited under sonic agitation favoring the hypothesis of increased mass transport.

B. Chronoamperometry

Figure 2 shows current transients for copper deposits at low temperatures. It can be clearly seen that the shape of the silent current transients changes as the temperature decreases.

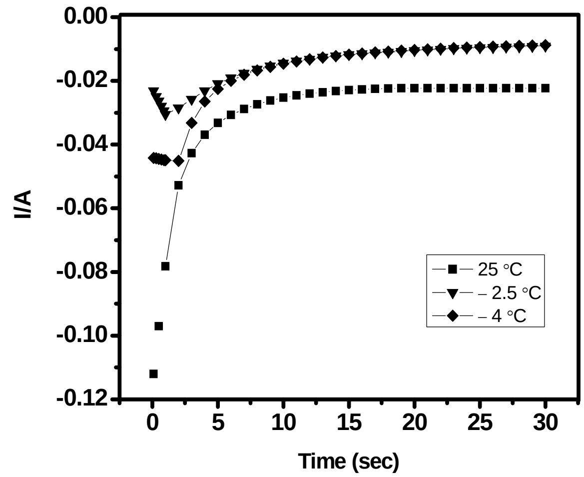

Fig. 2: Choronoamperometric Curves for the Nucleation of Copper at Different Temperatures under Silent

The silent current transient curves follow a maxima and decrease in current according to the Cottrell's predictions. Whereas the sonication transients have increasing and irregular plateau as shown in fig. 3. Calculation of characteristic kinetic parameters of the depositing parameters give diffusion coefficient values from $1.54 – 2.1 \times 10^{-5}$ $cm^2 s^{-1}$. The nuclei number density gradually increases from $1.45 – 3.98 \times 10^6$ cm^{-2} at decreasing temperatures.

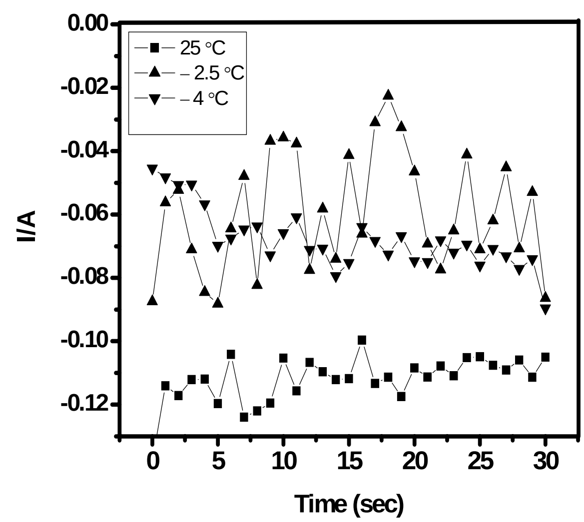

Fig. 3: Choronoamperometric Curves for the Nucleation of Copper at Different Temperatures under Sonication

Thicknesses of the films are calculated by the total charge consumed, and are below 1 µm (70 – 550 nm). Details of the analysis are given in Table 1. The dimensionless nucleation and growth curves are fitted to Scharifker-Hills model. At high temperature all the nuclei sites appear instantly whereas at low temperature the sites engulfed gradually in virgin condition. With ultrasound the nucleation sites are uncovered instantly; however, the already deposited nuclei may undergo crystal breakage in the intense energy field. Thus the broken sites could possibly provide sites for secondary nucleation [7].

TABLE 1: CALCULATED THICKNESS AT DIFFERENT TEMPERATURES

Temp in ◦C	Charge(C)		Film thickness (nm)	
	Silent	Sonication	Silent	Sonication
25	0.882	3.35	145.2	551.5
−2.5	0.518	2.04	85.3	335.9
−4.0	0.433	2.55	71.3	419.8

C. Phase Analysis

X-ray diffraction was used to characterize the copper surface. Figure 4 shows the spectrum for the copper deposits for sonicated samples at varying acid concentrations, temperature and copper concentrations respectively. It is indicated that the dominant diffraction peaks of FCC Cu-Zn (ICDD 25-1228) and brass (ICDD: 50-1333) [8,9] are clearly observed. Three main peaks at 2θ = 43.266°, 72.127° and 79.291° are attributed to the (330), (631) and (720) planes with (330) being the most intense are detected.

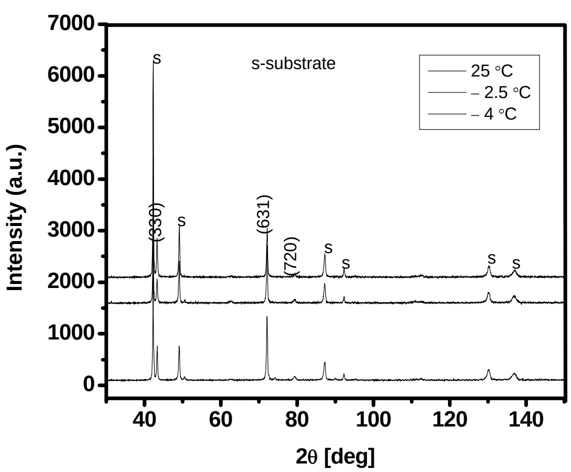

Fig. 4: XRD Pattern for the Cu Films Deposited at Varying (a) Acid Concentrations, (b) Temperatures

As the film thickness are below 1 μm, the X-ray beams might have penetrated to the surface more pass the coating resulting the Cu-Zn compound identification and not the pure copper.

D. Structural Analysis

The structural difference by morphological studies between the investigated coating systems at varying temperatures for both silent and ultrasonic conditions can be detected from figures 4-6. The application of ultrasound was found to affect the rate and mechanism of Cu deposition, and also the morphological detail of the deposits.

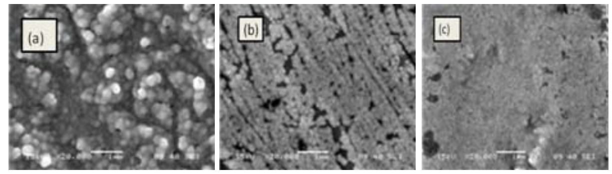

Fig. 4: SEM Photograph of Silent Deposit at Magnification ×20000 for Different Bath Temperature (a) 25^{0}C, (b) -2.5^{0}C, (c) -4^{0}C

The SEM images under sonication display that there is good surface coverage, good crystallinity and no crack in the surfaces of the films. The film deposited at – 4 °C comprises of better uniform grain size and surface finish (micro rough) while at 25 °C deposits are much more rough and non-uniform. The deposit at – 4 °C contains traces of polishing lines also. A highly adherent deposit in ultrasonic conditions can also be observed.

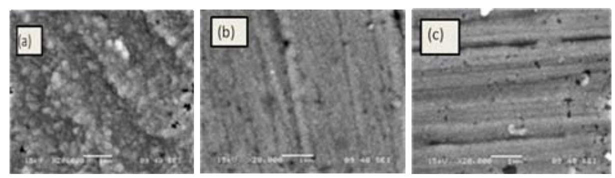

Fig. 5. SEM Photograph of Sonicated Deposit at Magnification ×20000 for Different Bath Temperature (a) 25^{0}C, (b) -2.5^{0}C, (c) -4^{0}C

However the deposits without sonication shows smaller grains and the population density has decreased at low temperatures as evident by the poor surface coverage. The shape and size of the grains of the sonicated copper samples are further analyzed by AFM studies as shown in Fig 6. The grains appear to be hemi-spherical or nearly spherical and highly agglomerated. The mode of agglomeration prevents the analysis and calcualtion of the size of the crystals. However, the maximum grains of deposit at 25 °C are in the size range of 200-400 nm with a maximum height of 376 nm and average roghness of 300 nm. Grains with maximum height of 91 nm are observed for copper layers deposited at lowest experimented temperature. The above effects of ultrasound in a highly supersaturated parent phase (low temperature) are based on the following facts. Low temperature favors nucleation ahead of growth. Ultrasound generally increased the rate of deposition, as analyzed by CV and CCT, except at small tip-electrode separations, where ablation was found to be a dominant factor. As such the increase in current under ultrasonic agitation might arise from the enhanced nucleation, enhanced growth or both. It has been mentioned by Floate et. al. that ultrasound affects growth rather nucleation [10]. However, we have observed the impact on both nucleation and growth and are far from conclusion. The application of ultrasound favors a more instantaneous nucleation behavior at all operating conditions. Such observations of changes to the nucleation behavior may result from an ablation effect of ultrasonic agitation that strips away newly formed/poorly adhering nuclei from the electrode surface and combined with the secondary nucleation on existing nuclei might result in fine grained adherent deposits at low temperatures.

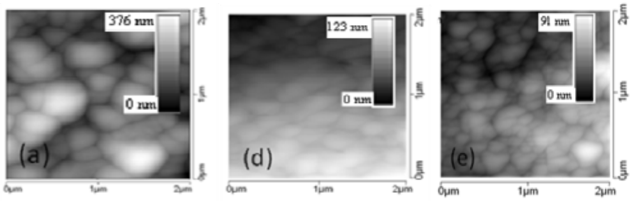

Fig. 6: AFM Micrograph of Sonicated Deposit for Different Bath Temperature (a) 25^{0}C, (b) -2.5^{0}C and (c) -4^{0}C

IV. Conclusion

Electrodeposition methodology under sonication presented in this work appears to be efficient to produce good quality metal films with special properties and thus has the potential of being exploited for both research purposes and industrial applications

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