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A perpetual evolution of electrochemically deposited nano-structured Cu thin films driven by acoustic cavitation

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Abstract:-The experiments described in this communication show how it is possible to tune the size of copper deposits when the depositing system is coupled with power ultrasound. The mechanism of sono-process has been analyzed and comments are made.

Key-words:- Copper, Thin Film, Electrodeposition, Cavitation, AFM, Choronoamperometry

1. Introduction

The nano-scale properties of copper and its alloys have found applications in catalysis, sensors, microelectronics and many other areas of nanotechnology that are currently dominated by the use of gold, silver, palladium and platinum nano-materials. Although there are number of processes to synthesize nano copper, but because of the propensity of surface oxidation of copper, few methods have been established. Among them, electrochemical technique is a simple yet powerful means to prepare nano-materials. And the use of high power- low frequency ultrasound in electrochemistry is a consequence of the useful effects coming from the cavitation events. The dramatic effects of acoustic cavitation for the size reduction of the materials to the nano-scale have already been established [1,2]. Electrocrystallization accompanied with acoustic cavitation has been ascribed to a momentary large increase in the degree of supersaturation, induced by the high transient pressures and temperature generated by a collapsing cavity [3]. Bubble collapse near an extended surface can also produce localized high-speed jets of liquid, acoustic streaming, which impinge on the surface. Hence, ultrasound can manipulate the crystal synthesis either by initiating primary nucleation and secondary nucleation, performing crystal habit and perfection, reducing agglomeration or a non-invasive alteration in sterile environments [4-7]. While the convincing hot-spot theory [3] explains well the creation of nano-structured products under cavitation, the incongruent aspect of abridged crystal agglomeration with the associated shock waves is still the object of a vivid scientific debate. Hence our work focuses on the arguments of description for the combined approach of the effect towards the macro- to nano- evolution.

2. Materials and Methods

Brass substrates of 1 cm^2 surface area were used to electrodeposit the copper films. The bath composition was 6.35 g L−1 $CuSO_4 \cdot 5H_2O$ + 60 g L−1 H_2SO_4. A three electrode open cell with

an Ag/AgCl reference electrode (Eco Chemie, Netherlands) and a platinum counter electrode (surface area of 3.14 cm^2) were used for the deposition. A high-density ultrasonic probe (Sonics & Materials, VCF1500) equipped with titanium oscillator (horn) 12.5 mm in diameter, operating at 20 kHz with a 20% output was used for ultrasonic irradiation. The cavitational threshold of the system was determined to be approximately 65 W cm^{-2}. The deposition were carried out with variable time periods for 5, 10, 15, and 20 s at a tip to substrate separation of 5 mm. Electrochemical measurements were conducted using a potentiostat/galvanostat (Eco Chemie Netherlands, Autolab PGSTAT 12) interfaced with a PC controlled with GPES software. A potential of −0.45 V (100 mV more than the estimated Nernst equilibrium potential: −0.35 V) was selected for the deposition. The surface morphology comparisons were obtained using JEOL 6480 LV scanning electron microscope (SEM) and SPMLab-programmed Veeco diInnova atomic force microscope (AFM) in the contact mode with a conducting p(n)-doped silicon tip.

3. Results and Discussions

The nucleation phenomenon corresponds to the initial stage of copper electro-formation. It can be considered as the most critical stage of growth for definition of the final film properties. And the analysis of the "current-time" curves at short times offers a suitable diagnostic tool to study Cu electrodeposition. The effect of ultrasonic irradiation on the *i(t)* curves is shown in figure 1 along with a virgin (without sonication) transient. In silent current transient, increase in current was observed and a maximum value is reached.

The current peak is followed by a decreasing part of the transient, which obeys to the typical growth current as that of Cottrell prediction. Under sonication the transients have quite different features. The *i(t)* curves have tapped current distribution after the first nucleation period. This current progression may not be inferred as noise (2s persistence). This leads us to advocate and argue that insonication transients consist of several of those nucleation and growth cycles [6].

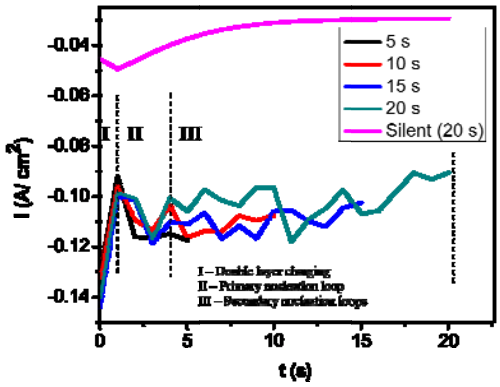


Fig.1. Chronoamperometri current transients for Cu deposits under insonation for different time periods

It is possible that the further nucleation in the continuously insonated case may be secondary, caused by solid small particles broken away from the crystal surfaces by the cavitation events. However, the abrupt decay in current following the nucleation phases does not envisage the growth rate of existing nuclei as per the model. Hence, the growth phase could have possibly been dominated by the nucleation surfeit. In order to determine the effect we calculated the values of diffusion coefficients (*D*) and other kinetic parameters from the plots as presented in Table 1. There are several published methods that utilize the coordinates of chronoamperometric curves to determine nucleation mechanisms and parameters related to nucleation, among which the model developed by Scharifker and Hills (SH model) [8] is the most widely used. According to the SH model, two limiting cases have to be considered:

Table I: Characteristic Kinetics Parameters of *i(t)* transients obtained for sonicated Cu deposits for different deposition time periods

instantaneous and progressive nucleation. Instantaneous nucleation occurs when the nucleation rate is very short and hence high. If the nucleation has a low value, nucleation will be progressive. A simple estimation of the extreme limits can be predicted by the slope of log(current density) vs log(time). We got the set of values (0.4-0.55) which support the instantaneous phase appearance. The kinetics parameters were then accordingly calculated using the general equation (Eq. (1)) for instantaneous nucleation.

$$I_{3D}(t) = \frac{zFD^{0.5}c}{\pi^{0.5}t^{0.5}}\left[1-exp\left(-N_0\pi kDt\right)\right] (1)$$

Where *z, F, c, N_0* and *t* are electrons involved, Faraday constant, bulk concentration of electroactive species, number density of active sites and time involved in the deposition process respectively. *k* is a dimensionless quantity $(8\pi cM/\rho)^{0.5}$, *M* and ρ are molar mass and density of the depositing species. Diffusion coefficient of the films can be calculated from Cottrell's equation (Eq.(2)).

$$I(t) = \frac{nFD^{1/2}C_0}{\pi^{1/2}t^{1/2}} (2)$$

The calculated diffusion coefficients of Cu^{2+} ions in static condition is 1.1×10^{-5} ($cm^2\ s^{-1}$) as compared to the values of $6.4\text{-}6.8 \times 10^{-5}$ ($cm^2\ s^{-1}$) for depositions with ultrasound. Values of *D* are affected significantly by the improved mass transport to the depositing substrate in presence of ultrasound. Hence, there should be effective impact on the nucleation population density. The calculated nuclei number density for primary nucleation, $N_{0\ (P)}$, for all the time period is approximately same. The number density for the secondary nucleation is increasing with increasing time period. However, the rate of increase of number of secondary nuclei decreases with time. The thickness of the films were estimated from the following equation (Eqn. (3)), assuming that two electrons are consumed for the formation of one molecule of copper and that no parallel charge transfer other than that leading to deposition of Cu is taking place at the deposition potential.

$$d = \frac{QM}{193000A\rho} (3)$$

Where *d, A, Q, M* and ρ are film thickness, film area, total charge passed during deposition, molecular weight of the deposit and density of the film respectively.

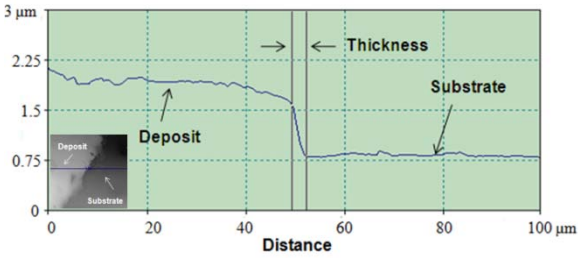


Fig. 2: AFM micrograph of sonicated deposit at 20 s (Thickness measurement)

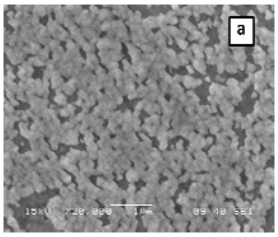
The peak and valley method of AFM analysis has been used to measure the thickness of the films (figure 2). The measured and calculated values are given in Table 2. The micrograph along with the line analysis also shows a nearly smooth and uniform deposit. Figure 3 shows the SEM micrographs of the above set of samples. It is evident that the surface morphology depends on the duration of sonication impact. It can be observed that sonication applied to perform deposition strongly affects the density of copper nuclei, adherence, their distribution and surface coverage. A less uniform particle size distribu-

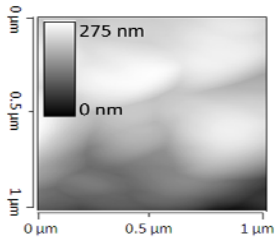
Time (Sec)	I_{max}(A/cm^2)	t_{max} (S)	D × 10^{-4} ($cm^2\ s^{-1}$)	$N_{0\ (P)}$ × 10^3 (cm^{-2})	$N_{0\ (S)}$ × 10^3 (cm^{-2})	$N_{0\ (T)}$ × 10^3 (cm^{-2})	Q_{total}(exp) C
5	0.116	3	6.6	1.52	–	1.52	0.764
10	0.114	3	6.4	1.56	3	4.56	1.1
15	0.118	3	6.8	1.48	4.2	5.68	1.69
20	0.117	3	6.7	1.5	6.1	7.7	2.05

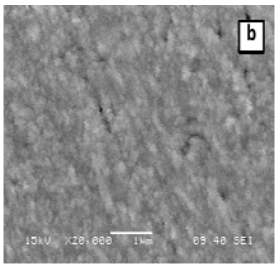
tion is noticeable for the shortest period of insonication. For the 759 nm thick Cu layer on top of brass, the surface is relatively smooth. As a means of gaining insight into the brunt of sonoelectrodeposition on these surfaces, the AFM images shown in figure 4, follow the further analysis of Cu depositions. The depositions appear as a slowly advancing front of the nanoevolution, without apparent change in the crystal habitat. It can be noticed that at 5 s the grains fall within the range of 210 – 260 nm height with a roughness factor of 49 nm. Sonication for more 5 s (10 s) the bigger grains appear to be agglomerates of 90 – 134 nm grains. As the time of deposition increases the standard deviation of the grain distribution becomes narrow and smooth. Deposition of Cu proceeds via homogeneous nucleation of

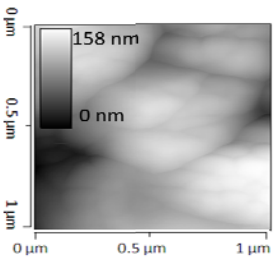
Table II: Roughness factor and grain size distribution from AFM measurements

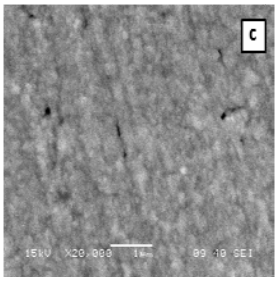
Time	Grain distribution (nm - nm)	Roughness factor (nm)	Average height (nm)	Thickness (nm)	
				Calculated*	Measured
5	210-260	47	201	280	266
10	90-134	23	100	405	418
15	50-80	19	60	624	612
20	10-30	15	42	757	759

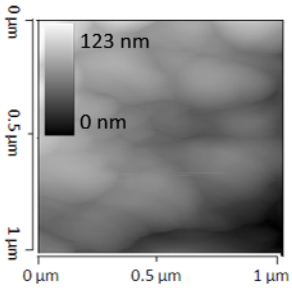


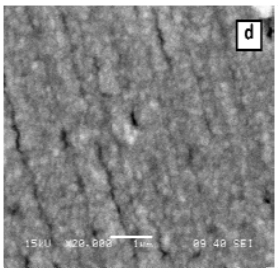












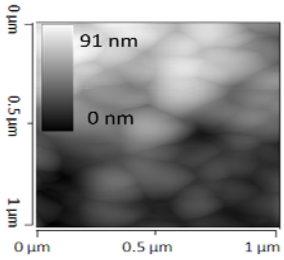


Fig. 3: SEM micrographs of sonicated Cu deposits

Fig. 4: AFM micrographs of sonicated Cu deposits

nanosized clusters with no preferential growth under 20 s ultrasonic impact. Most of the grains fall in the height range of 10 – 30 nm. A total analysis of the area and volumetric analysis is given in table 2. The possible explanations for the interesting observations are that the fast kinetics associated with the cavitation field might have not permitted the growth of the nuclei. Crystal fragmentation by ultrasound has possibly created new steps on the defect free crystal face to further supplement the crystallization process. The crystal breakage might have produced smaller grains and balances the heights of grains. This in result has smoothened and produceed finer grained depositions at longer period of deposition under sonication. Now pondering the crystal agglomeration by the generated shock waves, the growth of the nucleation centers due to inter-particle collision would have been limited to only embryonic surface fusion by the short cavity-collapse time. In return this has resulted a compact and adherent film on the brass substrate.

4. Conclusion

The combination of ultrasound with the electrolytic copper deposition system has been found to crystallize nano-structured copper thin films within a very small size range. The present theory suggests that this triggers the nucleation phenomenon by ultrasound assisted crystal fragmentation and negligible embryonic inter particle fusion. We have quantified the effects. The analysis of chronoamperometric curves confirms the 3D character of Cu deposits. The nuclei population densities were determined by the

Scharifker-Hills models. Our calculated data demonstrates increased diffusion and hence mass transportation under sonication. Crystal morphology and distributions have been identified by SEM and AFM. From the deposition transients and the analysis of size and spatial distribution, we can conclude that nucleation rate is fast in comparison to growth. Hence, cavitation being a nuclei dominated phenomenon, the scope of nano-evolution is unambiguous for prolonged sonication. It should be interesting in future work to study the structure driven properties of the copper films for various applications.

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