Implication of Low Temperature and Sonication on Electrocrystallization Mechanism of Cu Thin Films: A Kinetics and Structural Correlation

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The effect of an ultrasonic environment during electrodeposition of copper on graphite at various electrolyte temperatures of 25, 20, 15, 10 and 5 °C is reported in this investigation. Resulting Cu deposits formed by potentiostatic deposition were characterized by electrochemical methods, scanning electron microscopy and atomic force microscopy. It was found that in presence of ultrasound the deposition kinetics was mainly dominated by the charge transfer. Copper nucleated according to 3D instantaneous mechanisms for all temperature ranges. The extent of nucleation was found to be increased at low temperatures. Diffusion coefficients and nuclei population density were calculated for each temperature range. Sonicated deposits with good surface coverage were found to consist of spherical copper agglomerates of nanosized particles.

Keywords: *electrocrystallization, thin film, copper, low-temperature, sonication, crystal nucleation kinetics*

1. Introduction

It is scarcely surprising that, as the temperature is varied within the wide range available, the properties of all materials undergo very considerable modifications. Hence there are fundamental, analytical and technological reasons for the need of extending this temperature range for venturing into the relatively unexplored science[1,2]. Coupling ultrasound with the depositing bath may introduce a second level of metastability with a wide variation of effects on the deposit morphology and properties[3-6], resulting primarily from acoustic cavitaion: the formation, growth, and implosive collapse of microscopic bubbles in liquids[7-10]. Electrodeposition in presence of ultrasound may have effects on the deposits in terms of appearance, adherence, grain morphology and habitats. To cite few are, reduction in grain size[11], change in grain orientation with wave orientation[12], particle agglomeration and increased dispersion[13-15], brighter surface[16], reduction in residual stress and hence good adhesion[12,17] have been observed at constant frequency and power output. While with varying frequency and intensity, inconsistent fluctuations in the deposit behavior were also cited in the literature[12,18]. Authors have certainly enlisted the interesting beneficial synergistic effects. However, the findings are incompetent without proper information on the mechanism and kinetics of the phase formation. Electrochemistry at low temperature will likely be a diffusion controlled system whereas insonation may make a transformation of the plain system to a more complex one by introducing convective mass flow[12,19].

The present investigation focuses on the effects of temperature and ultrasound on the kinetics of Cu redox couple from the sulfate bath by using cyclic voltammetry, chronoamperometry and morphological analysis to understand the nucleation mechanisms.

2. Material and Methods

Graphite electrodes (Asbury, USA) of 0.25 cm² surface area were used to electrodeposit the copper films. Experiments were carried out onto single graphite electrodes for different sections of study. The bath composition was 6.35 gL^{-1} Cu^{2+} + 60 gL^{-1} H$_2$SO$_4$. Chemicals used were as purchased (Merck Chemical Co.). Double-distilled water was used throughout the experimentation for preparation of solution and other purposes. The electrochemical cell was a conventional three-electrode configuration, with a 5 cm long counter electrode of Pt rod (3.5 cm²) and a Ag/AgCI reference electrode (3 M KCl, Eco chemie). Regular glass beakers of 500 mL volume were used as the electrolytic cells for experiments with ultrasound. The sonication cell was having a water jacket with a temperature below the experimented electrolyte temperature. The arrangement was made to maintain a constant temperature during the sonication experiment. A high-density ultrasonic probe (Sonics & Materials, VCF1500) equipped with a 12.5 mm diameter titanium oscillator (horn), operating at 20 kHz with a 20% (1500 Watt max.) power output was used for ultrasonic irradiation. The working electrode was facing to the ultrasonic horn (Figure 1). Depositions were carried out at temperatures of 25 °C, 20 °C, 15 °C, 10 °C and 5 °C.
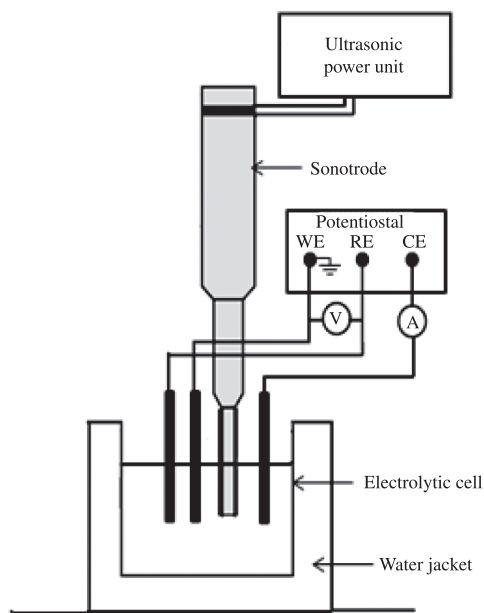
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Figure 1. A schematic view of the experimental set up for the electroplating of copper using a beaker as an electrolytic cell.

Figure 2. Cyclic voltammetry of copper redox reaction from a solution of 6.35 gL^{-1} Cu(II) and 60 gL^{-1} sulfuric acid at 25 °C in (a) silent and (b) sonication conditions.

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 –300 mV was selected for the deposition. The surface morphology comparisons were obtained using scanning electron microscopy (SEM, JEOL 6480 LV with Oxford data system) and atomic force microscopy (AFM, SPMLab-programmed Veeco diInnova) in the contact mode with a conducting P(n)-doped silicon tip.

3. Results and Discussion

3.1. *Cyclic voltammetry*

Figure 2 shows two voltammograms recorded during copper electrodeposition onto graphite substrates in (a) absence (silent) and (b) presence of ultrasound at a scan rate of 10 mV.s^{-1}. The scanning ranges are –0.6 V to +0.6 V and –0.6 V to +1 V for silent and sonication conditions respectively to ensure complete dissolution of the deposited mass in both the conditions.

The silent scan has both cathodic and anodic peaks, while the insonated CV has only the dissolution peak. During the sonicated cathodic scan, the reduction of copper ions has an onset potential near +50 mV *vs*. Ag/AgCl. Figure 2 also shows that, in anodic scan the anodic peak current for stripping or dissolution of copper on graphite is increased by 4-fold under insonation (Figure 2b) as compared to silent conditions (Figure 2a). Stirring of solution by the acoustic streaming during the sono-voltammetric scan may have hindered the depletion of electroactive species in the vicinity of the electrodes during deposition which has resulted the increase in cathodic and anodic currents. Moreover, the anodic peak potential also shifted to more positive values
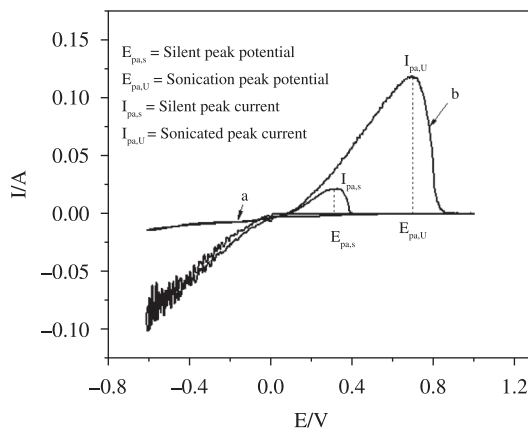
under ultrasound (20 kHz), $E_{pa,U}$ = +693 mV compared with $E_{pa,S}$ = +344 mV *vs*. Ag/AgCl in silent condition. So a ΔE of approximately +349 mV was found under sonication and this displacement of the anodic peak potential is most likely due to the Ohmic drop in the solution. And this may be manifested by the sonication effect on the rate of mass transport and other associated effects in the electrochemical bath[20].

In order to identify the kinetics and rate-controlling steps of the electrodeposition of copper, the investigation is now focused on the effects of low temperature and ultrasound (Figure 3a) on the variations of the voltammograms. All sono-voltammograms tends to have area of stability at high potentials i.e. a limiting current, which depends on the magnitude of the diffusion layer thickness[21,22], expressed as:

$$I_{\lim} = nFADC*/\delta \qquad (1)$$

where I_{lim} is the limiting current (A), n is the number of electrons transferred during the electrochemical process, F is the Faraday constant (96,500 C.mol^{-1}), A is the electrode area (cm^2), D is the diffusion coefficient (cm^2.s^{-1}), $C*$ is the concentration of the species in the bulk solution (mol.cm^{-3}) and δ is the diffusion layer thickness (cm). Furthermore the limiting current value can be used to calculate the mass transfer co-efficient k_d, from the formula, $kd = \dfrac{I\lim}{nFC}$, which characterizes the mass transport conditions from and/or towards electrode surface and, therefore, denotes a local measurement of the hydrodynamic conditions. The quantity varies from 5.9-6.54 × 10^{-3} with increase in temperature. Furthermore inside the cathodic zone ($E < 0$ V) of voltammograms, a crossover on the cathodic branches was observed during the reverse potential scan which in turn indicates the deposition of copper through a nucleation and growth phenomena. The potential crossovers are present at the anodic potential region.

Apart from the phase kinetic characterization, the cross over potential can be related to the equilibrium potential, in this case $Cu^{2+}(aq)/Cu(s)$ and this equilibrium
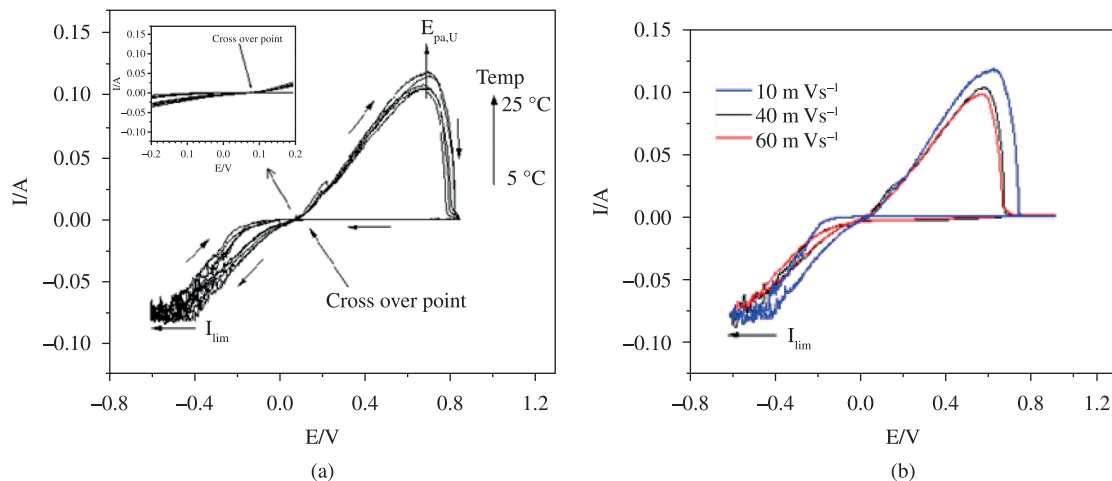
2013; 16(2)

Implication of Low Temperature and Sonication on Electrocrystallization Mechanism
of Cu Thin Films: A Kinetics and Structural Correlation

541

Figure 3. a) Cyclic voltammetry of copper redox reaction from a solution of 6.35 gL⁻¹ Cu(II) and 60 gL⁻¹ sulfuric acid at different temperatures in sonication condition. b) Cyclic voltammograms for graphite electrodes in 6.35 gL⁻¹ Cu(II) and 60 gL⁻¹ sulfuric acid at various sweep rates: 10 mVs⁻¹, 40 mVs⁻¹, 60 mVs⁻¹, at electrolyte temperature of 25 °C in sonication condition.

potential in sonication has turned out to be independent of deposition temperature. The CV scans have well-resolved anodic peaks without any cathodic maxima. The absence of cathodic peaks for the insonated working electrodes may indicate a charge transport control reaction system. Stirring of solution by the acoustic streaming during the sono-voltammetric scan may have hindered the depletion of electroactive species in the vicinity of the electrodes during deposition which has caused the above effect. Further to supplement the observation, a set of voltammetric study were done with different scanning rates[23]. The influence of the potential scan rate (v) on the Cu deposition at 5 °C is shown in Figure 3b. The scans reveal that with increase in scanning rate a decrease in peak height (I_{paU}) was observed in contrary to the conventional increase in peak values. The unusual negative peak shift with increasing scan rate, the positive potential crossovers and absence of cathodic peaks may signify well availability of the reducing species at the electrode/electrolyte interphase, and, therefore may imply charge (or interfacial) control kinetics.

To analyze the deposition efficiency of the process (the total coulomb of charge consumed during deposition, Q_c, charge consumed during dissolution, Q_a), the charges due to the cathodic and anodic processes are to be obtained from integration of the cathodic and anodic branches of the I-E curves, respectively. Figure 4 shows plot of the Q_a/Q_c ratio as a function of temperature for Cu deposition from solutions with sonication The Q_a/Q_c ratio reached a value of 1 as temperature dips further indicating the anodically dissolution of cu deposition during the cathodic sweep potential. Since all the deposited Cu has got dissolve by Faradic reaction (not by ablation), the deposits should have good adherence with the substrate.

3.2. *Nucleation and growth analysis*

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
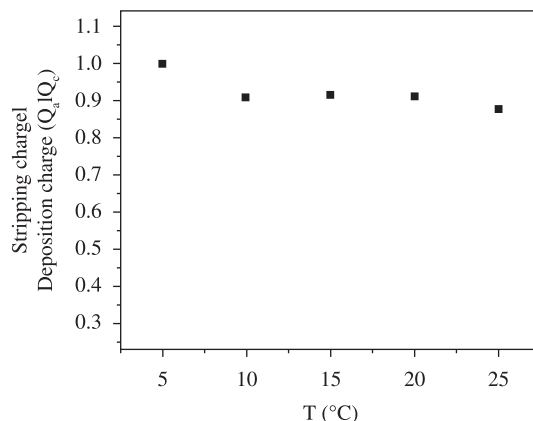

Figure 4. Stripping charge/deposition charge Q_a/Q_c for sonicated deposits as a function of deposition temperature.

properties. The most widely used technique to capture and quantify the kinetics is a single step constant over voltage scan, chronoamperometry (ca). Based on the cathodic zone of the CV experimentation the reduction potential, $E_c = -300$ mV, was chosen. The effect of temperature on i(t) curves were recorded during sonication copper formation.

Two-Point Golay–Savitzky normalization sono-chronoamperometry transients are shown in Figure 5. In presence of ultrasound and being emitted from a horn probe at a 5 mm distance from the working electrode, sonication was found to have random fluctuation in the observed current. The indiscriminate current variation results are similar to that of our previous work on the mechanism of nucleation in presence of ultrasound[24]. These current fluctuations are because of the continuous phase formation consisting of batches of sequential nucleation and growth cycles, the first being the primary nucleation and the rest are secondary nucleation on the existing primary nuclei due to crystal fragmentation. In each nucleation loop, the

current peak is followed by a decreasing part of the transient, which corresponds to the current limited by the diffusion of Cu(II) species. The crystallographic misfit between the graphite and Cu atoms may favor a 3D nucleation and growth behavior, since the surface of vitreous carbon consists of randomly oriented sp^2 carbon atoms, while copper atoms require ordered cryastallization in face-centered cubic geometry. Hence the Scharifker and Hills (SH) model was considered first in order to characterize the nucleation process[25]. The slope of log(current density) vs log(time) varied from 0.3 to 0.6, which indicates instantaneous phase appearance (as shown in Figure 6 for primary nucleation loop). Hence by applying the kinetics model we derived
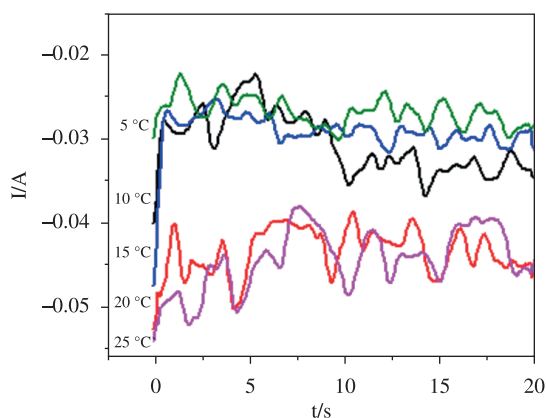

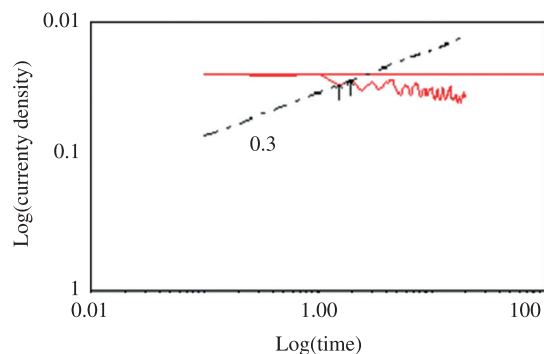**Figure 5.** Chronoamperograms of sonicated copper deposits as a function of temperature.

Figure 6. Log(current density) vs log(time) plot for sonicated Cu electrodeposition at –300 V for 20 seconds.

a 3D instantaneous mode of nucleation. A quantitative comparison of the temperature effect on the cavitation phenomena is represented in Table 1. The calculated nuclei number density (*N*) and diffusion coefficient (*D*) of the primary nucleation is taken into consideration as secondary nucleation would add some obvious data. Furthermore at high temperatures the fluctuations of these current was decreased. The variations of this mechanism with temperature can be explained on the basis of applied ultrasound intensity and the effects associated there. The authors have reported an increase of ultrasonic intensity of 134 W cm^{-2} to 177 W cm^{-2} as the temperature decreased from 25 °C to 5 °C[26]. In agreement with other reported happenings, the current spikes are found to be increased with increasing ultrasound intensity (here with decreasing temperature)[27,28]. Hence the cavitation process becomes more violent at low temperatures. As a result possibly there will be intense crystal fragmentation and localized supersaturation at reducing temperatures. Consequently the films may have better surface coverage and finer grain depositions, as both the effects of increased level of supersaturation and crystal fragmentation will trigger primary and secondary nucleation respectively. This possibility is better comprehended in the next section of morphological analysis. Now comparing the cathodic charges generated in the due process, there wasn't any regular variation in the quantity. This can be explained by a combination of increased number of intense nucleation cycles, rapid random changes in the surface ion concentration and ablation of material at the electrode surface.

Figure 7 shows the SEM micrographs of the sono-electrodeposited thin films. The original morphology of the particles is approximately spherical with the diameter varying between 400 nm and 1 μm. It also seems that each particle is composed of a series of small particles (in the range of 30-50 nm.) which can't grow separately and agglomerated to each other to form particles which are larger in size. Investigating on the surface coverage, sonoelectrochemically deposited films have good surface coverage. A nearly absolute coverage of the surface is achieved at 5 °C. In case of a complete coverage of the surface, the electrodeposition of Cu may follow two different mechanisms[29]. Firstly, the deposition occurs on the bare graphite surface and the formation of first Cu nuclei. At the initial stage, Cu is deposited preferentially on the surface steps and on the defects of graphite. Afterward, the nuclei population density increases and the Cu deposit expands on

Table 1. Kinetic parameters of copper deposition in presence of ultrasound.

Temp. (°C)	Kinetic parameters		Charge consumed (C)
	$10^{-4}D$ (cm².s^{-1})	N (cm^{-2})	Sonication
25	8.7	5.10×10^6	0.538
20	3.5	8.70×10^6	0.584
15	1.95	1.70×10^6	0.611
10	1.8	1.57×10^6	0.867
5	1.3	3.50×10^6	0.887

2013; 16(2)

Implication of Low Temperature and Sonication on Electrocrystallization Mechanism
of Cu Thin Films: A Kinetics and Structural Correlation

543

the totality of the surface. Secondly, a continuous deposition of Cu occurs on the freshly deposited Cu particles. Likewise these processes results in smoother uniform surface. Such control of the Cu particles distribution on vitreous graphite is only feasible if there is a continuous mass (ions) supply to the electrode/electrolyte interface (double layer). Hence the two path-ways are quite possible from a depositing bath where there is continuous stirring, extreme level of supersaturation (due to both temperature and sonication), possibility of secondary nucleation and the surface activation. However, the continuous surface cleaning (ablation) effect under insonation may rule out both the mechanisms and thus creating a zone of intricacy for uninterrupted instantaneous Cu phase nucleation and distribution. Now the nucleation path way followed in the due process can be explained from the data presented in Table 1. The percentage of

primary nuclei in sonicated condition has lead to a surface coverage of 60%, rest of surface occupancy could have been contributed by secondary nucleation. Hence insonation would have induced a nucleation mechanism which is combinations of the above two mechanism either occurring sequentially or simultaneously to form a superior deposit in terms of grain size, shape and distribution. Accordingly the best morphology with fine particles and good distributions was obtained for the deposit at 5 °C temperature. The surface profile and critical grain information are performed by phase mode ($-90°$ to $+90°$) AFM studies (Figure 8). The appearance of the deposits is similar to that of obtained by SEM experiments. Phase imaging goes beyond the simple topographical mapping to detect variations in composition, adhesion, friction, viscoelasticity, and numerous other properties. Here we coupled the phase mode micrographs
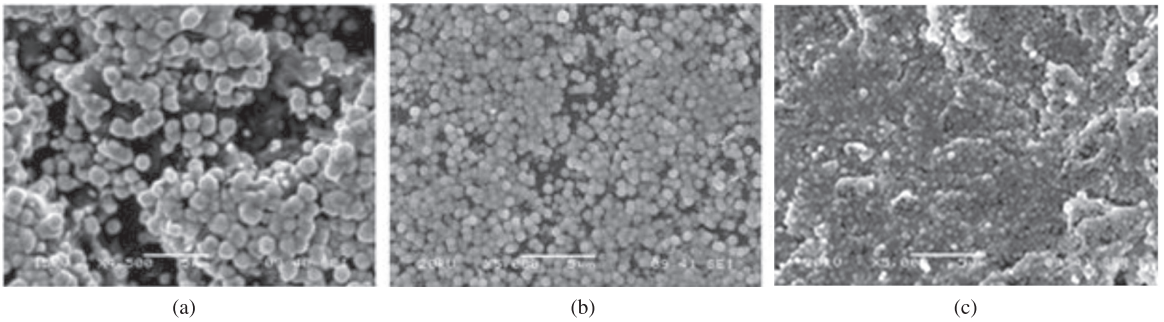

(a)   (b)   (c)

Figure 7. SEM micrographs of sonicated copper deposits at (a) 25°C, (b) 15 °C and (c) 5 °C.
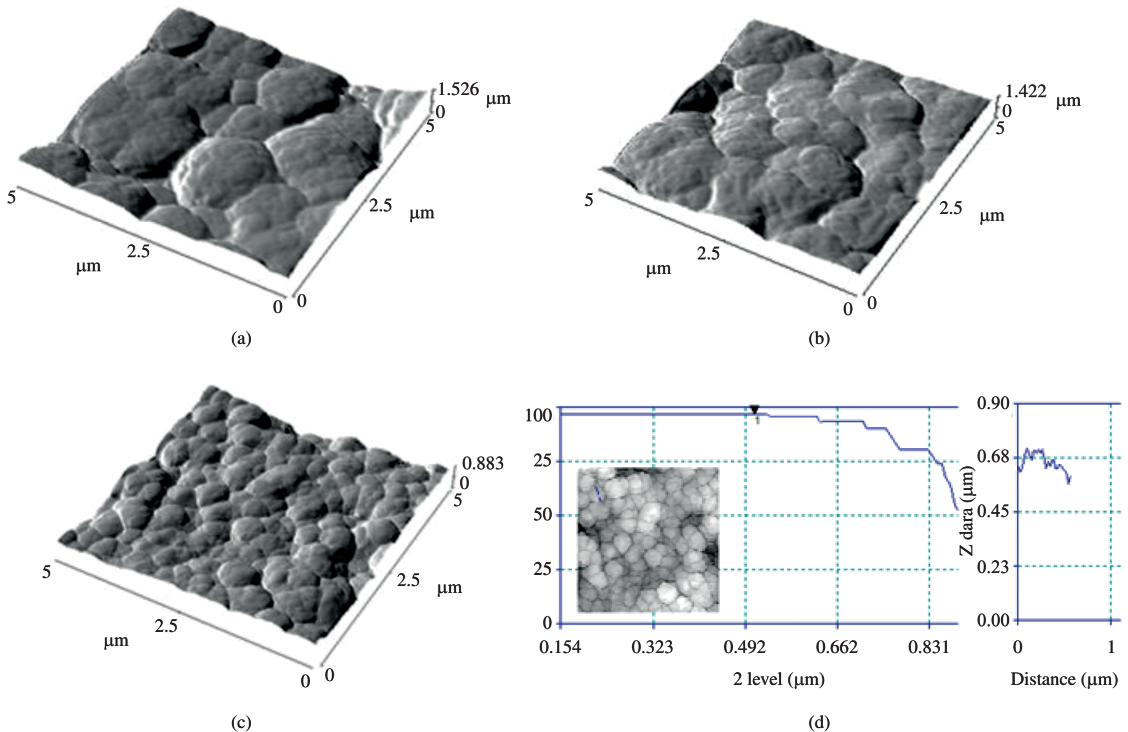

(a)   (b)

(c)   (d)

Figure 8. AFM phase micrographs of sonicated copper deposits at 25°C, (b) 15 °C, (c) 5 °C and (d) 2D micrograph with calculated BR and height profile at 5 °C.

Table 2. AFM analysis parameters of sonicated copper deposits at different bath temperatures.

Temperature (°C)	R_a(nm)		Critical dimension (μm)		Z level (95% BR) (nm)	
	Whole	Single	Whole	Single	Whole	Single
25	248	89	0.680	0.116	593	861
15	194	51	0.500	0.103	382	582
5	90	30	0.390	0.060	316	439

with the Z height instead of phase angle to visualize the surface uniformities in terms of their properties as well as their profile. The aggregation of fine particles to form the big spherical clusters can better be clarified from the figures. Except the cluster boundaries the inter-cluster regions are in phase, which means the surface is free of discontinuities in terms of contaminants and preferential growth (dendritic growth). Further a single particle scan for the deposition at 5 °C (Figure 8d) has been performed for a detailed study of the surface texture. The single particle of 360 nm size was found to be a coalescence of large number of small particles (of 40-60 nm size) with average roughness (R_a) of 30 nm. Bearing ratio (BR) analysis shows that, 96.5% of the total particle height is above 439 nm and only 2% above 800 nm which results a R_a of 90 nm for the whole surface. The definition of bearing ratio is the percentage of total data appearing above the selected Z level, hence higher the BR for the minimum Z level will be an analysis of smooth surface. Average roughness factor, Z level corresponding to 95% BR, critical dimension of bigger as well as the aggregating small particles for all deposition surfaces are presented in Table 2. R_a varies from 248 nm to 90 nm as the deposition temperature decreases. The table confirms the deposition at 5 °C to be of the highest surface finish. These observations may affect the state and intensity of depositing residual stresses and hence the de-lamination/adhesion characteristics of the deposited films onto the substrate[30].

4. Conclusions

Correlating the morphological investigations (by SEM and AFM) with cyclic voltammetry and chronoamperometry, the mechanism and kinetics of ultrasound assisted by low temperature copper elctrocrystallization has been tried to be portrayed in this investigation. The motive of decreasing temperature in presence of ultrasound while electrodepositing copper from a simple sulfate bath was to favor the nucleation. A positive anodic peak shift was observed for insonicated CVs. The redox process in sonication condition was mainly charge transfer controlled. The deposition efficiency of the system was found to be good, which could be due to the absence of simultaneous undesired cathodic reactions and good adherence of the deposits to the substrate. Copper nucleated according to 3D instantaneous mechanisms for all temperature ranges. The extent of nucleation was found to be increased at low temperatures. The addition of sonication has further assisted the nucleation process by stimulating the biphasic nucleation sequence i.e. primary nucleation due to the extreme high level of localized supersaturation at low temperatures and secondary nucleation by breaking the existing primary nuclei. The spherical copper grains were found to consist of nanometer sized agglomerates. However, the simple logic presented in the present study is in fact based on a complex mass transport issue which takes into account all the types of mass transportation including migration, diffusion and convection. Hence, whether the proposed mechanisms are the correct path-way for the discharge of the reacting species will remain unclear until investigations are tallied for the depositions down to one monolayer.

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2013; 16(2)

Implication of Low Temperature and Sonication on Electrocrystallization Mechanism
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545

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