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A Study on Ex-Situ Non-Isothermal Grain Growth Behavior of Sono-Electrochemically Deposited Cu Thin Films

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Abstract

In this work, the growth kinetics of low temperature sono-electrochemically deposited Cu thin films has been studied under non-isothermal conditions using a differential scanning calorimetric (DSC) technique. The analysis focuses on the effect of deposition temperature on the DSC results. The grain growth mechanism and mode were discussed by determining the variation of the activation and surface energies of the films. The kinetic observations were then correlated with the morphological evolution of the films using scanning electron microscopy and atomic force microscopy. The results suggest a transition of abnormal growth to normal mode of growth behavior as the film synthesis temperature was reduced.

Keywords: Grain growth, Thin film, Thermal properties, Sono-electrodeposition, AFM.

Introduction

Polycrystalline films have achieved their importance in decorative, protective, electronic, magnetic and optical devices and systems [1-3]. In all these applications their performance and reliability needs concern. There are various factors which influence their reliability, these may be related either to their structure or stress (intrinsic and extrinsic) or both including electromigration [4-6], stress induced voids [5,7], thermo-mechanical stress [8], delamination [9-11]. Another factor most widely researched is the growth behavior of the films which may affect the on-line film properties such as resistivity, hardness and stress. As for example, the resistivity of as-

deposited electroplated copper exceeds the bulk value by 10% - 30% but after growth of the film the resistivity decreases to near bulk values, the decrease is about 20% towards bulk value and lowering of hardness of grown film's by 40% [12,13]. The microstructural components contributing towards the above said growth behavior may include grain boundaries, stacking faults, dislocations, surface energy, elastic strain, pinning particles. However, the stored energy at the stacking faults, dislocations, elastic strain do not make a significant contribution in driving the growth phenomena [12,14] as comparison to grain boundaries and surface energy. Then again, depending upon the size and grain habitats there are quite a few established phenomena guiding the growth parable enlisted in Harper et. al [15] and the references there in. The mechanisms may lead two modes of grain growth i. e. normal and abnormal decided by the size and film relationship. If the grains grow just twice the thickness of the film, then the normal growth can be expressed for an isothermal temperature treatment as [16-18]

$$D^2 = D_0^2 + kt \tag{1}$$

where D is the mean grain diameter of the grains of grown films treated at different temperatures, D_0 is the mean grain diameter of the as-deposited film and t is the annealing time. The parameter K is written as [17]

$$K = \left(\frac{K^1}{T}\right)\exp\left(-\frac{\Delta G^a}{KT}\right) \tag{2}$$

where K' is a constant related with the interface energy density γ. The exp term and the T^{-1} dependence are related with the mobility M of the grain boundary. ΔG^a s the activation energy for atomic migration between grains, k is the Boltzmann's constant, T is the absolute temperature. To determine the activation energy for the atomic diffusion across the grain boundary during the grain growth, Kissinger equation act as a requisite tool [19]

$$\frac{E\phi}{RT_m} = An\left(1-x\right)_m^{n-1} e^{-E/RT_m} \tag{3}$$

where E is the activation energy, R is the gas constant, T_m is the peak temperature, Φ is the constant rate of temperature rise, x is the fraction reacted, A is a constant, n is the empirical order of reaction.

The normal grain growth is characterized by the steady state behaviour for which grain size distribution remains monomodal, self similar and has a time invariant shape. There exists another type of grain growth in which the grains grow abnormally, film's grain are many fold larger than the thickness value. This rapid and abrupt grain growth can only be explained in terms of a significant increase of grain boundary mobility. The grain boundary velocity behavior can be expressed as [17]

$$\upsilon = \left(\frac{C\Delta G}{TV_m}\right)\exp\left(-\frac{\Delta G^a}{RT}\right) \tag{4}$$

where C is a constant, R is the gas constant, T is the annealing temperature, ΔG is the difference in free energy between neighbor grains, ΔG^a is the activation energy for atomic migration between grains and V_m is the molar volume.

In the current investigation an attempt has been made to study the growth behavior of sono-electrochemically deposited copper thin films, as sonication has a definite impact on the film's physical properties. The growth thermodynamics and kinetics have been correlated with the structural studies to establish and propose the guiding mechanisms involved in the growth process.

Experimental

Copper films have been electrochemically deposited onto graphite substrates on an exposed surface area of 0.25 cm^2 at different electrolyte temperatures (25, 20, 15, 10 and 5 °C). The films were deposited on as received fresh substrates without any further treatment. Analytical grade $CuSO_4.5H_2O$ (6.35 gl^{-1}) and H_2SO_4 (40 gl^{-1}) were used for the preparation of electrolytes for copper deposition. The solution is prepared with doubly distilled water. The Electrochemical experiments were performed with a potentiostat/galvanostat (Eco Chemic Netherland, Autolab PGSTAT 12) system having computer interface of GPES software. A standard three- electrode cell was assembled with a counter electrode of Pt rod (3.5 cm^2, Eco chemie) and an Ag/AgCl reference electrode. The non-isothermal growth analysis was carried out using DSC (Mettler Toledo-DSC822). Experiments were performed at a temperature range of 25 – 400 °C at a temperature ramp of 5 °/min. For the calculation of activation energies, scanning rates of 10°/min, 20 °/min were used. Morphological studies of prepared samples were performed by means of SEM (JEOL 6480LV) and AFM (Veeco diInnova). The phase analysis was done with XRD (Philips x-pert MPD), and the patterns were recorded from 40-100° at a scanning rate of 2°/Min with CuKα radiation. The surface energy analysis was done in an OCA-20 Data Physics contact angle instrument.

Results and discussion

DSC analysis

Film thickness was varying in between 375 nm to 1 µm for deposition temperatures 5 °C to 25 °C respectively. Fig. 1a shows the thermograph of electrodeposited thin films at scanning rate of 5°/min. from 25°C- 400°C. The entire DSC traces exhibit either one or two exothermic heat release peaks at around temperature of 300 °C. High (25-15 °C) and low (10 and 5 °C) temperature films have two and one exothermic peaks respectively. The exothermic peak signifies the occurrence of grain growth where due to the average increase of the grain size decreases the grain boundary area or the grain boundary energy. This decrease of grain boundary energy can be confirmed from heat release during the exothermic reaction which is supported by the upward peak (exothermic peak) during the thermal scan. The peak temperature and the associated heat release is higher for 5 °C as compared to other temperatures. This may be due to

the fact that majority of the grains are small sized, so require higher temperature to attain equilibrium for their growth and simultaneously will release more heat than the coarse grained deposits. Along with exothermic peaks some unsystematic endothermic peaks have also been observed for 10 °C, 15 °C and 25 °C at various heating rates. The energy consumed for these depressions in the DSC scan can possibly be due to the reaction of nitrogen (the reacting atmosphere in the DSC furnace) with the carbon substrate resulting in an amorphous product during DSC experimentation [20]. The presence of nitrogen in the samples after DSC run was confirmed from the EDS elemental analysis as shown in fig. 1b. To study the kinetics of grain growth i. e. to determine the activation energy for grain growth, the samples were scanned at different heating rates. The DSC thermographs are shown in fig. 2a for the temperature of 25 °C. At low heating rates, the systematic orientation controlled growth will ease the early attainment of equilibrium. While at high heating rates the random grain growth will be far from equilibrium because of lack of any order. So the peak temperature for the high heating rates is generally greater than for low heating rates. The effective activation energies from the thermograms for grain growth (equation 3) can be obtained from the slope of a straight-line fit to a plot of $\ln(\Phi/T_m^2)$ versus $(1/T_m)$. The calculated effective activation energies for grain growth (from equation 3) is given in fig. 2b. The values signify a grain boundary self diffusion growth mechanism as observed by other researchers [15]. However the variation in the energy values is not uniform. This variation of the activation energy might be attributed to the grain size and orientation even though it is not known how they can induce such fluctuations. Each thermal analysis was scanned at least twice to ensure authenticity. No definitive answer can be found at this point. To elucidate the growth mode for the grain boundary driven self diffusion growth, a set of surface energy analysis was done before and after DSC treatment and are given in fig. 3. Surface energy was found to be increased for temperatures 25, 20 and 15 °C whereas for the other temperatures there is a decrease of the values. The above discrepancy may be attributed to a transition from abnormal grain growth to normal growth with reduction of temperature, which can be correlated with the multi peak observations in the DSC scan for the above temperatures. These growth kinetic observations are then correlated with structural evolution to envisage and explain the issues further.

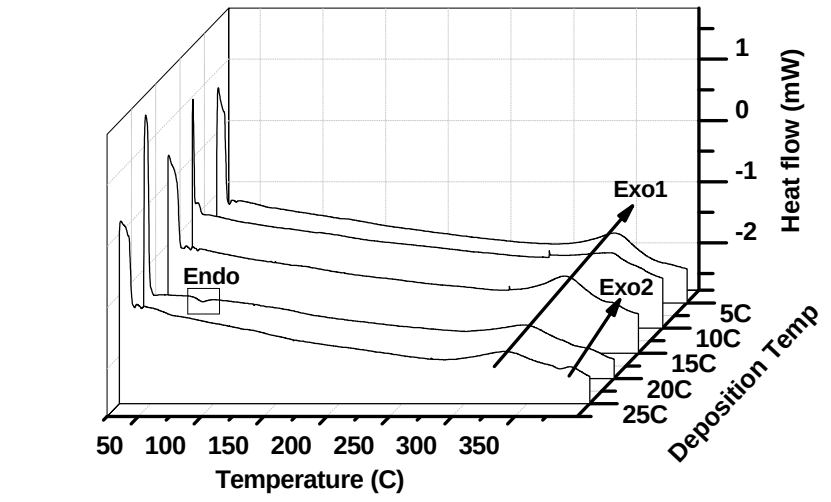
XRD analysis

The XRD patterns of the as-deposited and after DSC scan of copper films have been illustrated in fig. 4. The sharp peaks show the crystallinity of the copper deposits. The diffraction peaks at 2θ = 43.27, 50.34 74.132 and 89.934 can be indexed as the (111), (200), (220) and (311) planes of copper with cubic symmetry respectively [21]. The intensity of peaks of as-deposited films decreases with decrease in bath temperature as shown in fig. 4a. This attributes to the formation of smaller sized grains at lower bath temperature compared to the higher one. Although after thermal treatment the spectrum is quite noisy, peaks corresponding to copper lattice systems can be observed. The intensity of the peaks corresponding to copper has been reduced and has broadened too. An interesting finding can be observed here that the peaks have shifted towards left of 2θ (from 43.27° to 43.436° for Cu(111)) values to that of

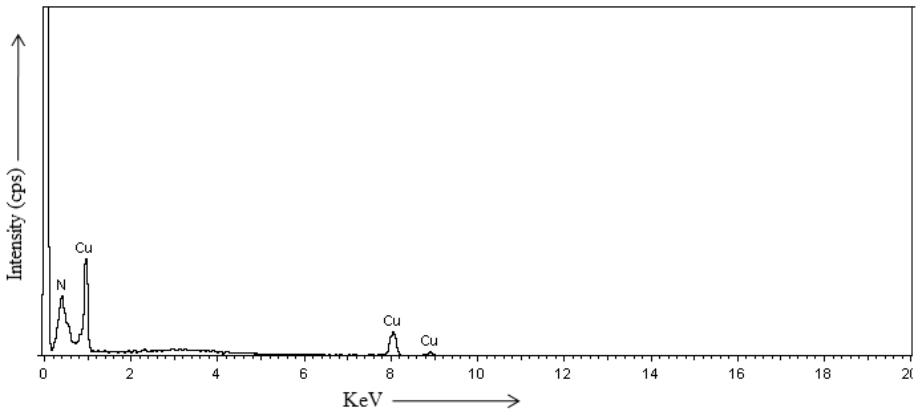
observed values in case of as-deposited copper. The reduction in intensity and broadening of the peaks may not be contributed by the particle size reduction. However, the reason for the inverted peak intensity variation and peak shifting is not clear, but this may be the consequence of the strain developed or generation of stacking faults and twins due to the growth of the grain. The crystallite size and lattice strain calculated from the XRD plots by using the Williamson- Hall method [22] is presented in fig. 5. The analysis of the XRD pattern in fig reveals that the crystallite size decreases (from 160 nm to 20 nm) and the associated strain increases as the synthesis temperature of the films was lowered. After thermal treatment all the grain size was observed to be increased and the lattice strain has got decreased.

Morphological analysis

Fig. 6 shows the SEM topographies of copper films before and after thermal treatment for the deposits prepared under sonication at – 300 mV for different bath temperatures. The as-deposited copper nuclei bear the spherical shape with varying grain distribution (fig. 6a-c). The size of the grains decreases with decreasing bath temperature. Due to the effect of intense ultrasonic irradiation and high level of supersaturation at low temperatures, agglomerated copper spheroids of size in between 400 nm to 1 µm are formed. Now concentrating on the SEM micrographs (fig. 6d-f), of the samples heated upto 400 °C at a temperature ramp of 5°/min., it can be visualized that after the thermal treatment, grains are bigger than their untreated counterparts with blurred grain boundaries. The distinct features of the surfaces of the treated films prepared at 25 and 15 °C are a bimodal grain distribution, small grains of 100 to 200 nm are observed on the very large grains. Whereas the low temperature films after DSC treatments have nearly uniform grain distributions on the surfaces. To enumerate the above observations, a detail study was then done by AFM (fig. 7a-d) for temperatures of 25 °C and 5 °C with two magnifications. The surface of 25 °C film at 20 μm^2 scan area is seen to have higher elevation (max. 5.317 µm) than the 5 °C deposit (max. 4.856 µm).While the corresponding images (Fig. 7b&d) at high magnifications show a drastic change in the morphology following an opposite trend, smoother topography at 25 °C temperature. The roughness values of the treated surfaces vary from 771 to 128 nm. The possible reasons can be conjectured at this point: the abnormality in the growth behavior could rely upon the size difference of the grains in the films, primary and secondary grains, due to the crystal breakage induced by ultrasound as reported by authors [23]. The size difference in the grains will reduce as the primary grains gets finer at low temperatures. Hence, the tendency of secondary grain growth would have minimized and the abnormal growth of fine grained smooth layer might have not happened for films deposited at low temperatures.

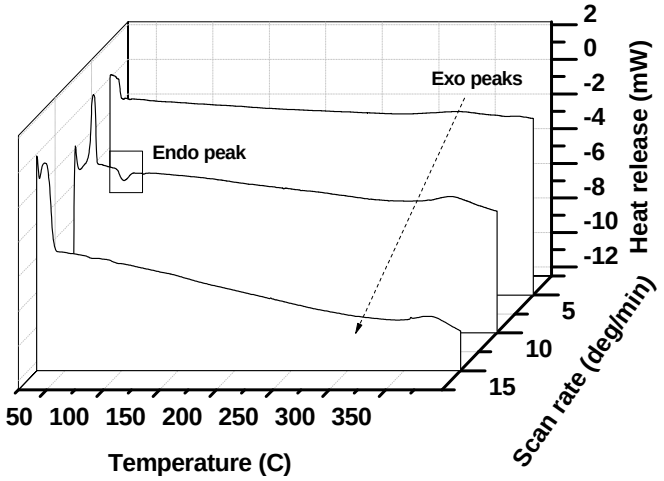


(a)

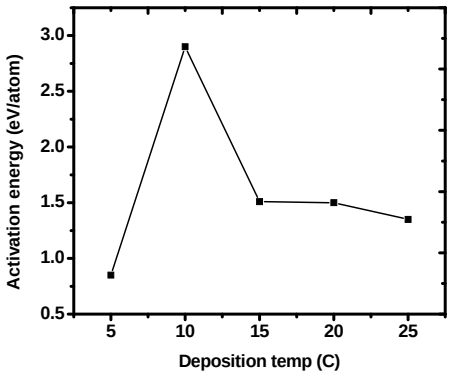


(b)

Figure 1: (a) DSC scans of copper deposited at different temperature at scan rate of 5°/min from 25 °C – 400 °C (b) EDS plot of post treated DSC Cu film



(a)



(b)

Figure 2: (a) DSC scans at heating rate of 5°/min, 10°/min, 20°/min of copper electrodeposited at 25 °C (b) variation of calculated activation energies for different deposition temperatures

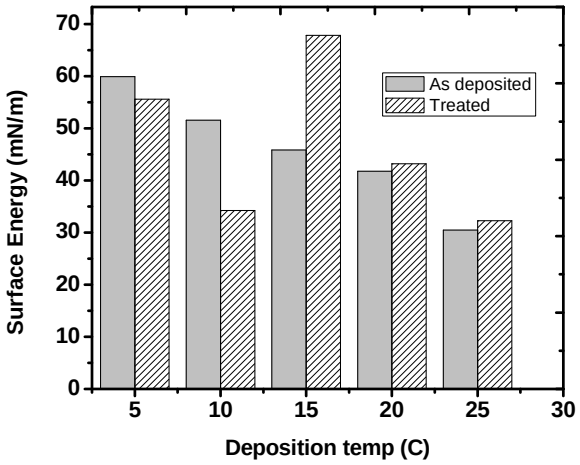
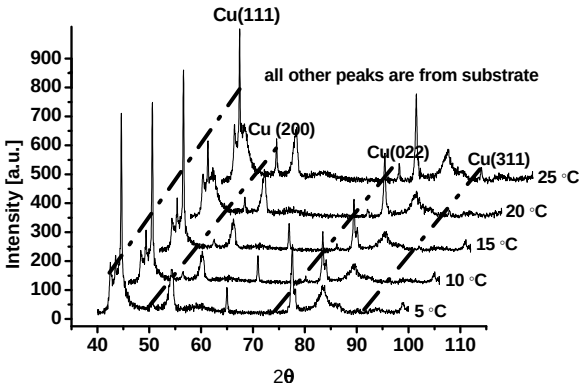
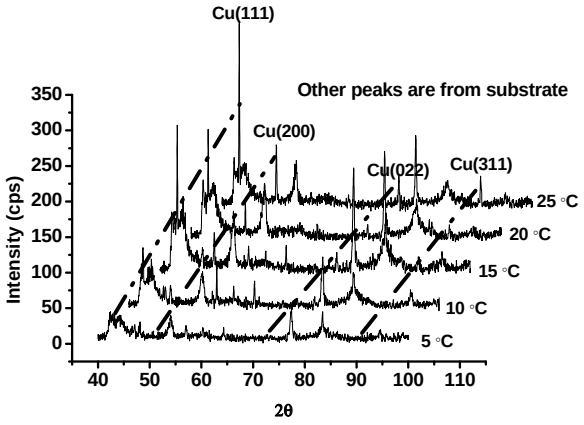


Figure 3: Variation of surface energy for Cu films in as-deposited and treated conditions deposited at different bath temperatures



(a)



(b)

Figure 4: XRD patterns of copper deposits under sonication condition (a) before and (b) after DSC treatment.

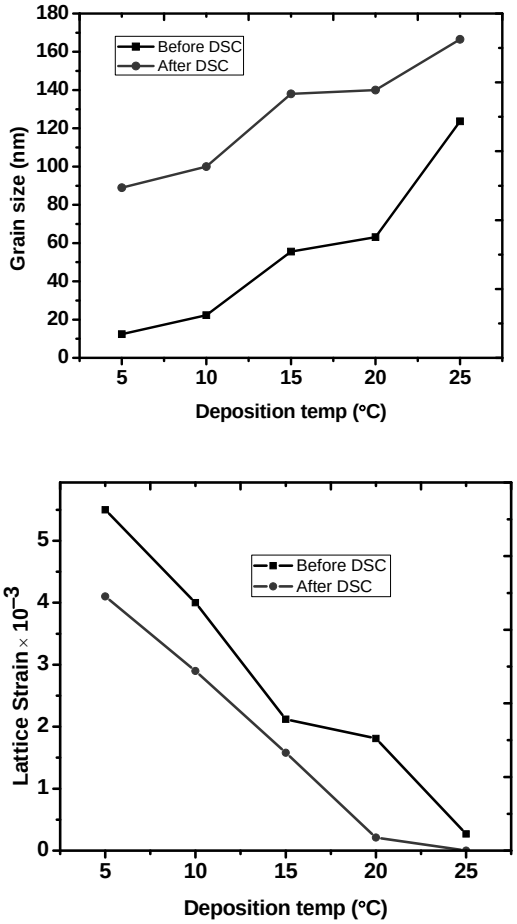


Figure 5: Variation of (a) crystallite size and (b) lattice strain with deposition temperature for as-deposited and treated films.

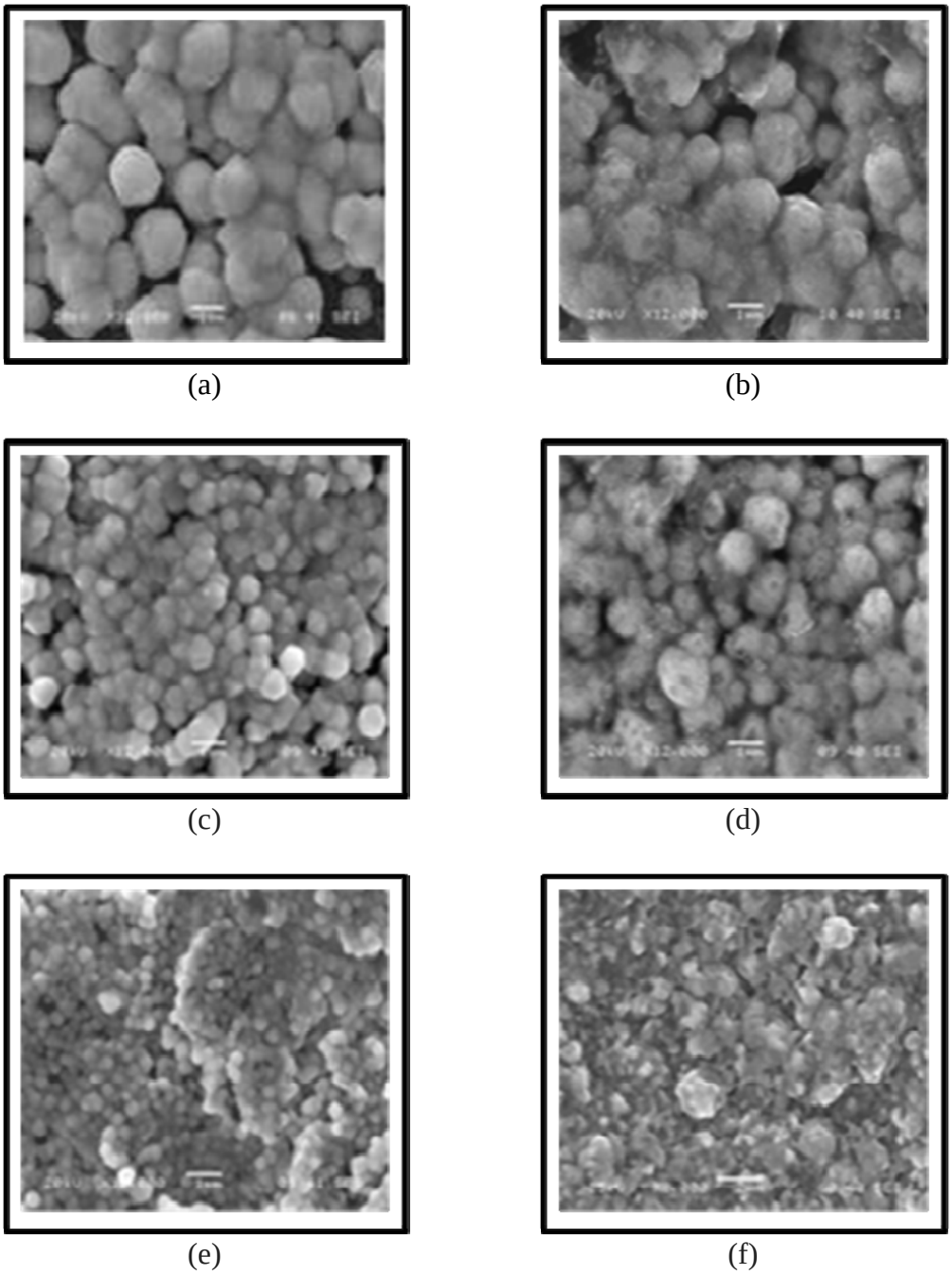


Figure 6: SEM images of as-deposited copper at (a) 25°C (b) 15°C and (c) 5°C temperatures and their corresponding micrographs (d) – (f) after DSC at heating rate of 5°/min.

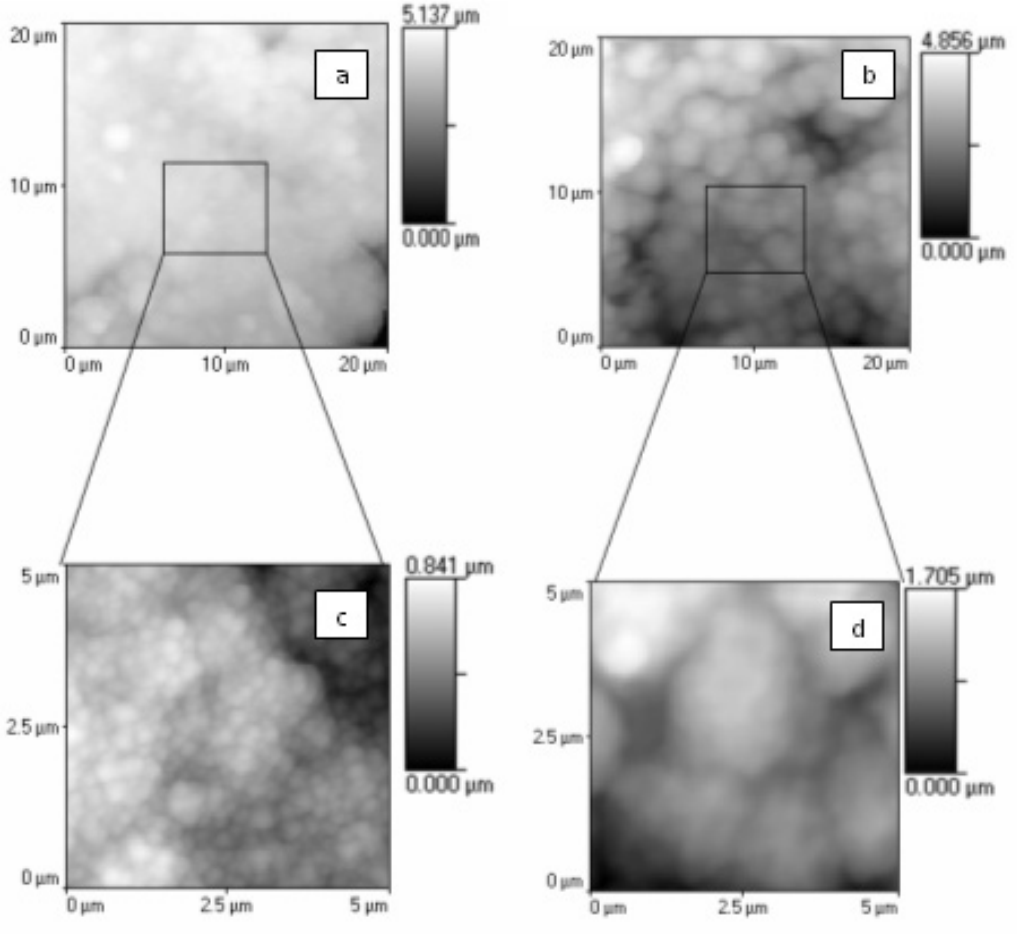


Figure 7: AFM micrographs of deposits of (a,c) 25 °C and (b,d) 5 °C temperatures after DSC scan

Conclusion

Thin films of Cu were prepared by sono-electrodeposition at reduced bath temperatures. The effect of bath temperatures and sonication on the non-isothermal post deposition growth behavior was investigated by examining the growth kinetics and condition of the surface microstructure by DSC, SEM and AFM. DSC thermograms were found to have multi and single peaks for high and low temperature films respectively. The applications of Kissinger method at several heating rates allowed to estimate the activation energy for growth, and was found to be controlled by grain boundary self diffusion for all the film crystallization temperatures. Results obtained for XRD and surface energy estimations of the films for both the conditions of as-deposited and post thermal treatment, have distinct variations. Comparisons between the DSC, surface morphology and texture analysis by SEM and AFM may suggest a transition of abnormal growth to normal mode of growth behavior as the film synthesis temperature were reduced.

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