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Morphological study of electrodeposited copper under the influence of ultrasound and low temperature

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ABSTRACT

The effects of temperature and cavitation on the electrochemistry principle were experimented here by adding the impact of sonication to synthesize ultrafine grained deposits at low temperatures. The X-ray diffraction analysis and microscopic studies confirmed the nanorange deposit. Scanning electron microscopy images have also confirmed the powdery and highly scattered deposits in silent conditions. Ultrasound was found to have a significant effect on the deposit morphology. The deposit obtained was compact, uniform and adherent. Energy dispersive spectroscopy result of the deposits revealed an oxidized silent deposit along with some adsorbed sulfur onto the electrode surface. In contrary the in situ cleaning associated with sonication has resulted in cleaner deposits.

1. Introduction

Electrodeposition is mostly used to obtain metallic films of adequate thickness, structure and adhesion. The high selectivity of the deposition processes allows uniform modification of surfaces and structures with complex profiles [1]. Accordingly, the effects of plating baths, plating modes, conditions as well as the effect of post-treatment on the textural characteristics of metal deposits are worthy of being studied [2,3]. Copper electrodeposition has been widely used in electronic industry for manufacturing of printed-circuit boards, interconnects, multilayer sandwiches of giant magnetoresistive hard disc read heads, protective and decorative coatings.

Electrochemical nucleation and growth are complex phenomena. The formation of deposit is dependant on time and flux. Fast mass transport causes the formation of many nucleation sites and the high flux contributes to the growth phase of the deposit [4]. Thermodynamics and kinetics of the process may depend on a number of factors. Existence of an energy barrier makes nucleation a probability process [5,6], with a rate

$$J_0 = Z_0 W \lambda^{-1} \exp\left[\frac{-\Delta G(n_c)}{kT}\right] \quad (1)$$

where, Z_0/cm^{-2} is the number density of active sites on the substrate, W/s^{-1} is the frequency of attachment of single atoms to the nucleus and λ^{-1} is a non-dimensional quantity accounting for the difference between the quasi-equilibrium and the stationary number of nuclei, $\Delta G(n_c)$ is the maximum energy barrier at a critical cluster size n_c, k and T have their usual meanings. The energy barrier that the ions have to surmount for an adatom formation is an obvious function of temperature. Decreasing temperature increases the level of supersaturation. Hence, the activity of ions will increase and the critical nucleating condition will occur at low temperature. The relationship between morphology and degree of supersaturation is an open area of research. However supersaturation determines the degree of metastability in the parent phase. To relate the non-equilibrium cluster energetic and fluctuational growth to the rate of nucleation, it is necessary to describe the cluster population distribution. The metastable equilibrium concentration of critical clusters of a given size, C_n, is then [7]

$$C_n = C_1 \exp\left[\frac{-\Delta G(n)}{kT}\right] \quad (2)$$

where, C_1 is the number of atoms per unit volume in the liquid. Thus a high nucleation rate can be achieved at low temperature.

The growth of clusters past the critical size can be represented kinetically [5,6] as:

$$J = \nu_{SL} S_{cr} C_n = \nu \exp\left(\frac{-\Delta H_d}{kT}\right) S_{cr} C_1 \exp\left[\frac{-\Delta G(n)}{kT}\right] \quad (3)$$

where, ν_{SL} is the jump frequency of atoms from the liquid to the critical cluster (it can be estimated from lattice vibration frequency ν

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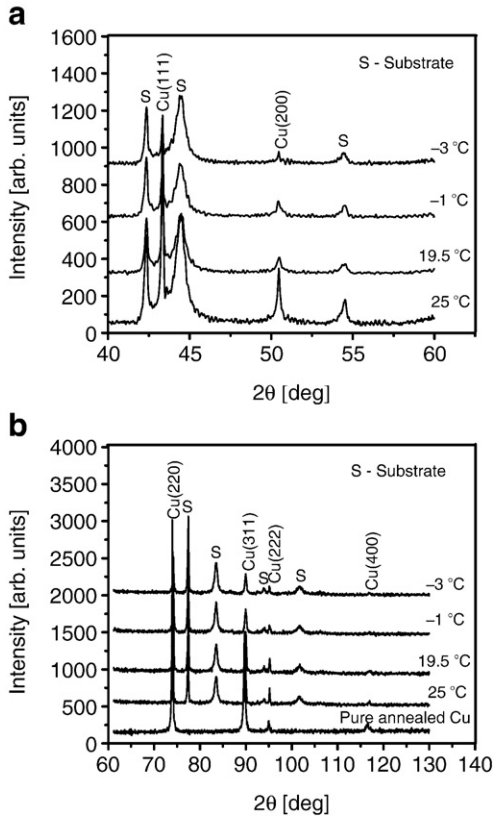

Fig. 1. XRD patterns of copper films prepared by sonication at different temperature at low and high 2θ values.

and activation energy barrier for interfacial diffusion ΔH_d), S_{cr} is the number of atoms surrounding a cluster and C_n is the number of critical clusters. At low temperature, the population of critical clusters increases whereas the rate of attachment of further atoms to the cluster decreases due to increased diffusion barrier. Hence temperature can affect the crystal growth by several ways, all of them predominantly resulting in a smaller crystal size at low temperatures [8,9].

Acoustic cavitation is the phenomena of sequential formation, growth and collapse of microscopic bubbles (voids) in the liquid [10,11] in the presence of an ultrasonic field. This sequence can produce temperatures as high as those on surface of the sun and pressure as great as those in the bottom of the ocean. Thus cavitation, by concentrating the diffused fluid locally in a very short duration creates a zone of intense energy dissipation. The sequential cavitation phenomena will thus create an extremely high level of localized supersaturation, resulting in triggered nucleation [12]. It has been proposed by various investigators that cavitation of electrolyte by acoustic streaming causes fast mass transport [13–15], degassing [16,17] and in situ cleaning [15,18] at the electrode surface. An extensive review on the versatile use of ultrasound in an electrochemical context has been given by C. E. Bank and R. G. Compton [19]. Ultrasound is also capable of inducing crystal breakage. This may further enhance the nucleation process by secondary nucleation. Remarkable increase in mass transport, the most distinct effect of cavitation, enables it to modify a diffusion controlled system to a charge transfer system [20,21]. Contribution of cavitation, thus, should affect nucleation more rather than growth. However increase in mass transport may also possibly affect grain growth. Hence the dominance of opposing effects of sonication and thermal environment are more likely to be contradictory and far from its conclusion.

The above mentioned effects of temperature and cavitation on the electrochemical crystallization principle are investigated in the present study. Electrochemical nucleation and growth phenomena are mainly quantified by electroanalytical measurements like potentiometry, voltammetry, polarography, coulometry and chronoamperometry. The present experiment aims here to prove the conventional hypothesis by different microscopic techniques and X-ray diffraction (XRD) method.

2. Experimental details

Copper was potentiostatically deposited from a simple aqueous solution of $CuSO_4$ (10 g l^{-1}) and H_2SO_4 (40 g l^{-1}) in an open cell. Double distilled water and analytical grade chemicals were used. Saturated calomel electrode was used as the reference electrode. Electrodeposition was done in a fixed over potential range of 100 mV to 600 mV at a sweep rate of 1 mV/s onto rough graphite electrodes from a pure copper anode. Temperature ranges selected for the above experimentation are 25 °C, 19.5 °C, −1 °C and −3 °C. A freezer was used to maintain low temperature conditions. Experiments were performed in the absence of antifreezers to avoid/minimize convoluting complications by the presence of foreign particles. An ultrasonic cleaner of 30 kHz frequency, with 60 W power with an inbuilt thermostatic heater of 0.04 kW was used for sonication impact.

Several techniques have been used to characterize the deposits. XRD patterns were recorded from 30° to 140° with a Philips X-pert MPD system diffractometer using Cu K_α at an accelerating voltage of 40 kV. Data was collected at a counting rate of 1°/min. The K_α doublets were well resolved. Crystal size was estimated by the well established, Williamson–Hall [22] formula applicable for adherent deposits. Microscopic studies to examine the morphology, particle size and microstructure were done by a JEOL 6480 LV scanning electron microscope (SEM) equipped with an energy dispersive X-ray detector of Oxford data reference system. Micrographs were taken at an accelerating voltage of 5 kV for the best possible resolution from the surface rather than the interior of the deposit. Energy dispersive spectroscopy (EDS) spectra were recorded at an accelerating voltage of 20 kV and the real collection time was around 1 min. A SIEKO SPA 400 atomic force microscope (AFM) with a silicon probe was used to take the AFM figures. The micrographs presented here are in non-contact imaging mode.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of the samples synthesized at different reaction temperatures are as shown in Fig. 1. Decrease in either domain size or lattice strain will cause effective broadening of diffracted peaks [23]. To clearly illustrate the broadening effect, XRD patterns are represented in two parts. Fig. 1(a) shows the low angle regions of the sonicated deposits. The peak pattern shows high crystallinity of copper along with peaks from the substrate material. The diffraction peaks at $2\theta = 43.27, 50.34$ can be indexed as the (111), (200) planes of

Table 1
XRD grain size and lattice strain of sonicated copper deposits.

Temperature in °C	Grain size in nm	Lattice strain
25	210	0.005
19.5	28	0.021
−1	22	0.024
−3	6	0.070