

Archived in Dspace@nitr <http://dspace.nitrkl.ac.in/dspace>

**International Conference in Advanced Materials and Composites
(ICAMC-2007), Trivendrum 24-26th of October**

Organised by NIST-CSIR

**LOW TEMPERATURE SONOELECTRODEPOSITION OF
NANOCRYSTALLINE COPPER DEPOSIT**

A.Mallik, R.N.Chauhan and B.C.Ray

Dept. of Metallurgical and Materials Engg., National Institute of Technology, Rourkela 769008 ,
India

E-mail-archananitrkl@gmail.com (A. Mallik – Corresponding Author)

ABSTRACT

This paper investigates copper deposit from a simple aqueous solution at sub-ambient temperature in presence of ultrasound. A highly adherent, lusterous, dense and fully sintered layer of copper deposit with cluster sizes between 40-70 nm are confirmed by SEM and AFM studies. The X-ray diffraction pattern confirms the copper crystallinity and the preferred growth orientation is the (1 1 1) direction. The melting property of the deposit was studied by a heating microscope. Softening started around 700°C as compared to the temperature of 900°C of commercial pure copper. To investigate the growth behavior of the deposit a 50 hours run by modulated temperature DSC was performed on the deposit. This result indicates that all the mechanism has occurred inside the solution. So it may be expected that the synergistic effect of low temperature, hydrogen evolution, over potential, high plasmon resonance leading to surface melting and high localized temperature and pressure may lead to such deposition.

INTRODUCTION

Electrodeposition as a means of materials synthesis offers the 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 can not be accessed by traditional processes [1]. Nucleation and growth processes in electrochemical metal deposition determine the physical, chemical, electric and magnetic properties of metal deposit. However, electrodeposition of metals can produce deposits with very different morphologies of pulverulent deposits, dendrites, needles, rough or porous deposits by changing sometimes slightly, the experimental conditions [2]. Thus nucleation step is required not only for the formation of a new crystal (3D nucleation) but also for the growth of a perfect singular crystal face by formation of new layers (2D nucleation). The birth and subsequent growth of the nucleus needs a certain degree of saturation. Nucleations may formed either [3] by simultaneous discharge of hydrated metal ions and incorporation to the kink sites or discharge at steps and then diffuse to kink sites or discharge while crossing the double layers and randomly be transferred to the native or foreign substrate. The competition between growth and nucleation determines the surface morphology and properties. The formation of an atomic nucleus

of the new phase requires one to overcome a thermodynamic barrier called Gibbs nucleation work. The nucleation work is connected with the transfer of ions from the ambient phase (the electrolyte) to the substrate surface under action of overpotential (extent of supersaturation) and excess free energy due to the creation of new interfaces when a nucleus appears on the electrode surface. The work is governed by the availability of active nucleation sites is an obvious function of overpotential, solution composition and concentration and substrate surface free energy [4]. The existence of a nucleation barrier makes the nucleation a probability process giving the lowest Gibbs free energy of formation to highest rate of cluster formation. Hence the process of nucleation is naturally either a mass transport or charge transfer phenomena.

The charge transfer rate for most metal reactions is sufficiently high for the continued growth of established or mature nuclei to be mass transfer controlled at moderate concentrations. The phenomena of diffusion and temperature are complimentary. The high temperature metal deposition condition is having less number of big colliding and overlapping growing centers due to the high mass transfer flux advancing radially much more rapidly than the perimeters what is forming the well known diffusion zones of diffusion fields. The condition somewhat approaches towards instantaneous nucleation with less number of fast growing centers. So growth may dominate nucleation. Where as low temperature may avoid undesirable interdiffusion between adjacent layers and structures and allows uniform modification of surfaces and structures with complicated profile. Though at low temperature with variable overpotential range the condition is for progressive nucleation there will be more or less progressive attenuation because of low mass flux rate. Thus there may be an opposition of high nucleation rate, because of decrease in thermal barrier with increasing degree of supercooling from ambient, to that of decrease nucleation. The effect is due to the reducing surface charge transfer overpotential. Sonoelectrochemistry, electrochemistry in presence of ultrasound, underlies on the phenomena of repeated formation and collapse of micro-sized cavitation bubbles [5]. On collapse the highly compressed bubbles release tremendous amount of temperature and pressure. It also agitates the liquid by shearing. It has been proved by various investigators that cavitation of electrolyte by acoustic streaming cavitation causes fast mass transport [6] and degassing at the electrode [7]. As the formation of deposit is time and flux dependent, fast mass transport causes the formation of many nucleation sites (small overlapping diffusion spheres) and the high flux of materials contribute towards growth. Now electrodeposition/plating under the influence of ultrasound, the critical effect is the increase in mass transport, which may be high enough to change diffusion controlled system into a charge controlled system. Ultrasound also ablates materials [8] from the electrode surface, but has no effect on growth via charge transfer electrode due to the metal ion.

SYNTHESIS

Electrodeposition is used as a route to fabricate copper nanoparticles. The deposition was commenced in potentiostatic mode. The electrolyte used was a mixture of CuSO_4 ($\text{Cu} = 10\text{g/l}$), H_2SO_4 (40g/l) and rest water at various temperatures. Doubly distilled water and analytical grade chemicals were used for the electrodeposition of copper. Before each scan and subsequent experiments, the electrodes were polished. The potential range applied for the deposition varied between 0.1V to 0.6V with reference to SCE at a scanning rate of 1mV/s. The dissolution of copper plate and deposition on graphite electrode has taken place in the working potential range for each respective temperature. During electrodeposition the electrolytic solution was not stirred.

CHARACTERIZATION

Several techniques have been used to characterize the electrodeposits and sonoelectrodeposits at various temperatures. X-ray diffraction (XRD) patterns of the electrodeposits were recorded with an Philips X-ray diffractometer using CuK α radiation ($\lambda=1.54\text{\AA}$). Scanning electron microscope (SEM) at low acceleration voltages, & atomic force microscope (AFM) were employed to examine the morphology, particle size and microstructure of the electrodeposits and sonoelectrodeposits at the various temperatures. Melting property was studied by a Leica heating microscope (0-1700 $^{\circ}$ C). A new and innovative sample preparation method was followed for sample preparation. The electrodeposited sample was smoothly cut into the required pellet size and was kept inside the microscope. The result was compared with a pellet sample of pure copper powder.

RESULTS AND DISCUSSION

The X-RD patterns of the sample synthesized at different reaction temperatures at sonication condition is shown in fig.1. The X-RD pattern reveals that the peaks correspond to characteristic peaks of cubic copper lattice (JCPDS file no.04-0836) of (111) and (200) planes. Along with copper there are some peaks of carbon (due to the substrate material), sulphur (from the electrolyte) peaks are also there. The pattern also reveals that the decrease in temperature, intensity decreases where as broadening increases though not in regular fashion. The broadening of peaks can be attributed to small particle size and strain of crystalline materials. Using the method developed by Williamson and Hall [47], the contributions of the particle size and strain to be observed X-ray line broadening, β , are considered to be additive.

$$\beta_{\text{total}} = \beta_{\text{particle size}} + \beta_{\text{strain}}$$

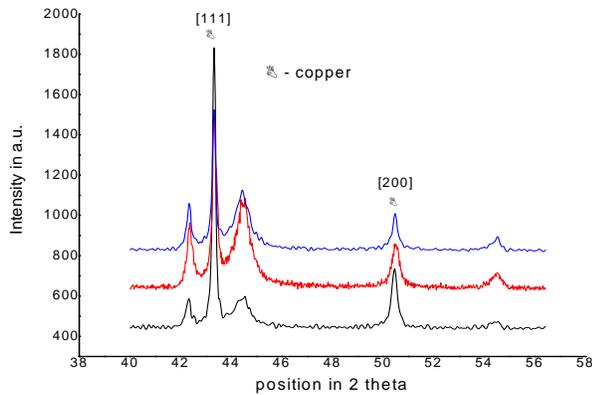


Fig. 1. XRD patterns of copper electrodeposits at various temperatures

The contribution of broadening due to small particle size is given by Scherrer equation while the broadening due to strain is represented by differentiation of Bragg's law.

$$\beta_{\text{total}} = \frac{0.94\lambda}{t \cos \theta} + 4 \tan \theta (\Delta d/d)$$

The total broadening (β_{total}) is the measured FWHM total in radians, corrected for instrumental broadening. The X-ray wavelength of the source (CuK α 0.154nm) is given by λ , t is the particle size, and $\Delta d/d$ represents the strain. Multiplying both sides of Eq.(2) by $\cos \theta$ gives the final form,

$$\beta_{\text{total}} \cos \theta = \frac{0.94\lambda}{t} + 4 \sin \theta (\Delta d/d)$$

which is used to calculate the particle size and strain for copper from a plot of $\beta_{\text{total}} \cos \theta$ versus $\sin \theta$. Using the y-intercept obtained from linear regression of the broadening as a function of diffraction angle, we obtained average particle size ranging from 1-14nm.

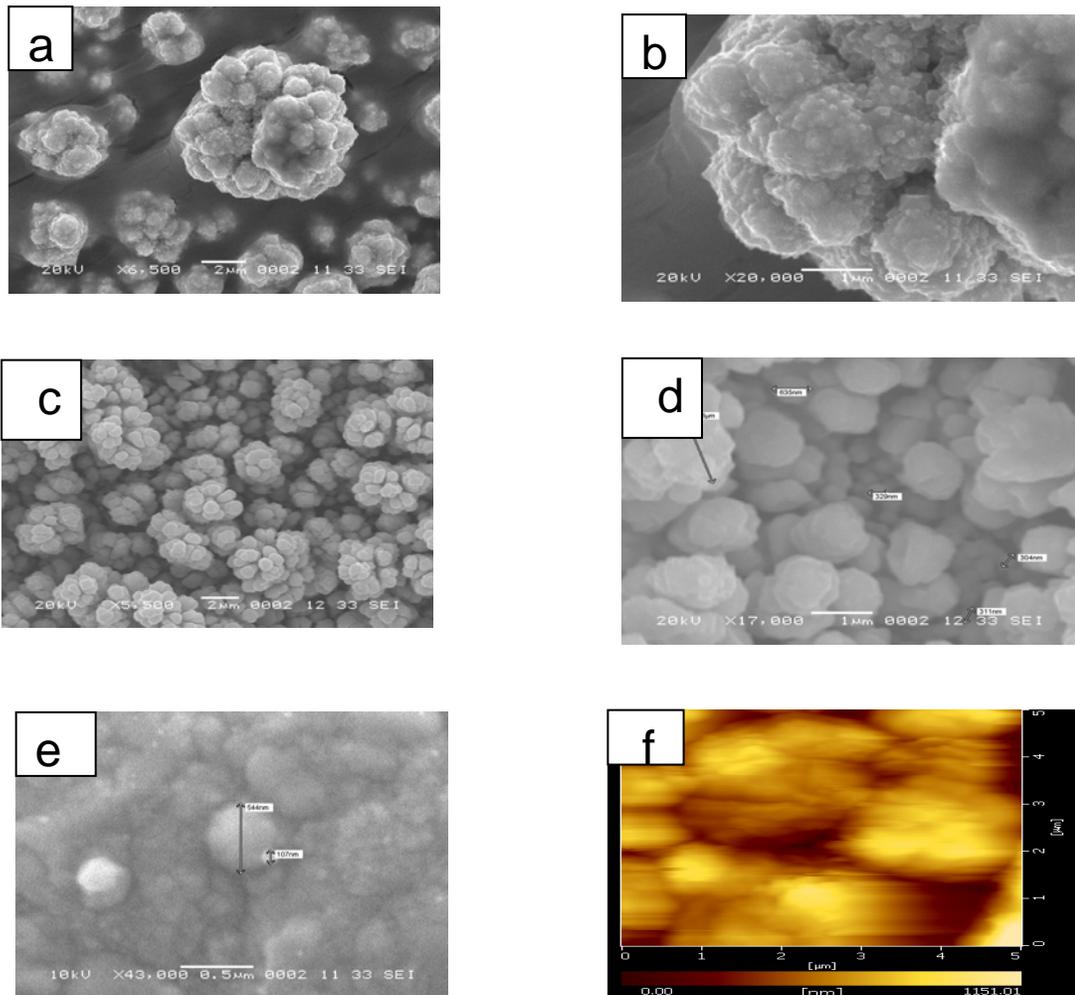


Fig. 3. SEM micrograph of copper deposits at (a&b) 5°C, (c&d) 2°C , (e) -3°C and (f) AFM micrograph at -3°C

Fig.2. shows SEM micrographs of the deposits at both lower and higher magnifications. There is clear indication of increased dispersion with reducing temperature. At 5°C copper has been deposited in the framework of cauliflower bud makeup with a non-uniform distribution. Substrate was not fully

covered by the deposit. Nanosized agglomerated spheroids of copper are organized in proper fashion as that of the cauliflower configuration. It seems that at 2°C buds have been fully untied and population has been increased to an extent of fully covered copper deposit. The deposit also gives a powdery impression. At -3°C the electrocrystallization has resulted even crystallization of copper domains.

High degree of aggregation has led to a firm and adherent morphology. A close look on the deposit is giving the amount of agglomeration. Decrease in temperature helps in increasing the activation of species i.e. supersaturation. Hence it may be assumed that ultrasound has helped in proper distribution of the mass. Plasmon resonance will increase to a great extent in nano region. In presence of ultrasound the interparticel collision may well occur. This will lead to surface melting. Copper, a highly reactive metal is having always tendency towards agglomeration. Fig. 4. shows an AFM image of the deposit at -3°C. The micrograph shows agglomerated clusters of an average size of 50-60nm.

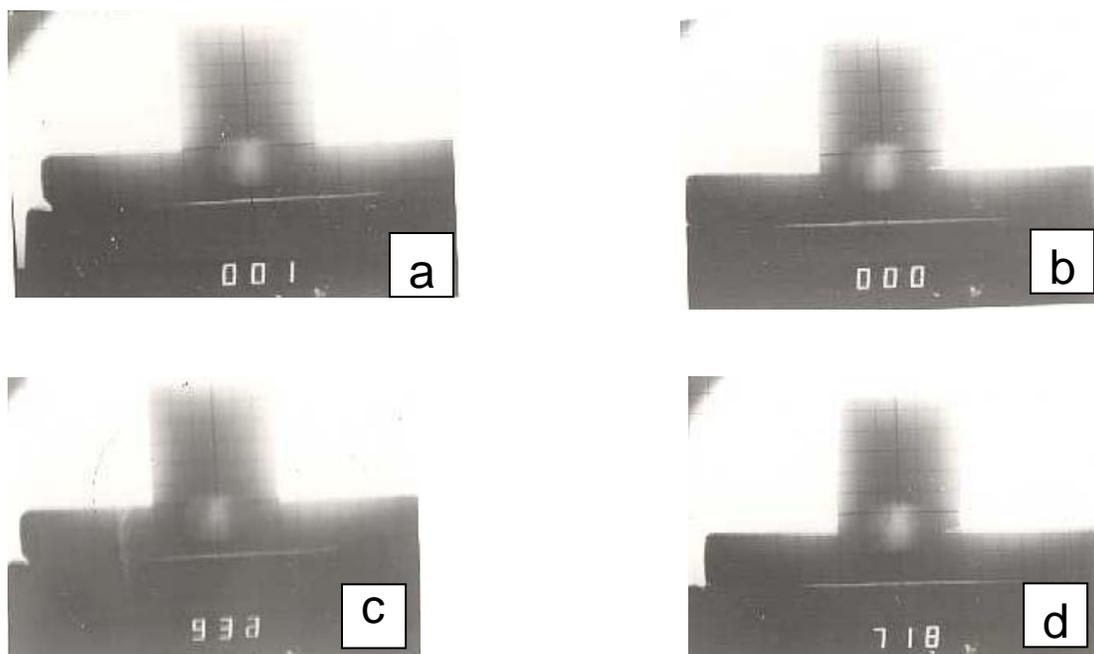


Fig.4. Sample condition in heating microscope (a&c) pure copper (b&d) eletrodeposit

To further compliment the above proposed mechanism a rough visual estimation (Fig. 5.) was done by a heating microscope. As the deposit is in graphite substrate a minute change on softening has been observed as that to the pellet of pure copper powder. Softening point of the deposit can be noticed at around 720°C as compared to 900°C of pure copper which is a bit in higher as compared to the 400-500°C range in literature. This gives the indication of grains in the nano range.

As explained earlier the unique deposit may be due to the synergistic effect of simultaneous localized high pressure and temperature from sonication, low bath temperature, hydrogen evolution, high surface plasmon resonance with increasing interfacial region and tendency for reduction in surface free

energy for greater stabilization. The first three phenomena strongly indicate that something has happened inside the electrolyte during deposition and the last two for conditions, though may be applicable inside the bath also, after deposition. Well to clarify the above mess an attempt has been made to study the room temperature growth by a modulated temperature differential scanning calorimeter (ADSC). The temperature setting was done at room temperature with a deflection of 0.5°C to catch even a small energy deviation in terms of temperature. Figure 5. shows the trend after keeping the specimen for about 60hours. It can be seen from the figure that there is hardly any change in the graph. Thus we may reach at the conclusion that, room temperature growth has not taken place. The extensive study in this area has been reported [9].

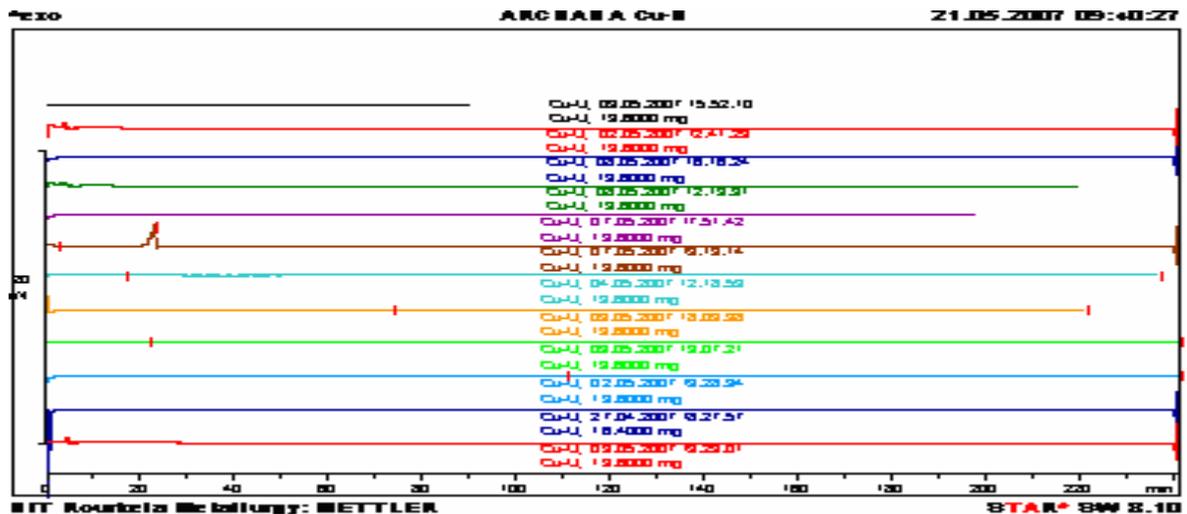


Fig.5. ADSC curve of copper electrodeposit

CONCLUSION

An attempt has been made to explore the low temperature electrochemistry in synthesizing nanoparticle with an ultrasound cavitation condition. The crystallinity and morphology of the deposits have been characterized by X-RD, SEM and AFM. With decreasing temperature the deposits approach nano dimension. Nano regime was again confirmed by the study of melting properties. To come up with a comment a modulated temperature DSC, having alternating heating and cooling mode of operation, experiment was performed to study the room temperature growth. The growth morphology of deposit is believed to be dependent more on solution condition.

REFERENCE

1. U. Erb, A.M. El-Sherik, G. Palumbo and K.T Aust, *Nanostructure Materials*. 1993, vol.2, pp. 383-390.
2. S. Glasstone: An introduction to Electrochemistry, 1st ed. East-West, Madras, 1942, pp. 482-485.
3. S. Nageswar, *Electrodeposition and Surface treatment*, 1975, vol.3, pp. 417-433.
4. A. Milchev and L. Heerman, *Electrochimica Acta*. 2003, vol.48, pp. 2903-2913.
5. P.R. Birkin, D.G, Offin, P.F. Joseph and T.G. Leighton, *Journal of Physical Chemistry B*. 2005, vol. 109, pp. 16997-17005.

6. K.B. Holt, J.D. Campo, J. S. Food, R.G. Compton and F. Marken, *Journal of Electroanalytical Chemistry*, 2001, vol. 513, pp. 94-99.
7. H. Yanagida, *Ultrasonic Sonochemistry*. 2007, Article in press.
8. F. Marken and R.G Compton, *Electrochimical Acta*. 1998, Vol. 43, pp. 2157-2165.
9. A. Mallik and B.C. Ray, “*Impact of ultrasound and low temperature during electrodeposition of copper*”, To be communicated.