

CHARGE TRANSFER VS MASS TRANSFER MECHANISM IN ELECTRODEPOSITION OF COPPER THIN FILMS: A STRUCTURAL EXPLORATION

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF**

BACHELOR OF TECHNOLOGY

in

METALLURGICAL AND MATERIALS ENGINEERING

by

SABYASACHI PANDA (108MM016)

SOURAV PATTANAYAK (108MM043)



DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

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UNDER THE GUIDANCE OF

PROF. ARCHANA MALLIK



DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING

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ROURKELA

2012



National Institute of Technology Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "**Charge Transfer vs Mass Transfer Mechanism in Electrodeposition of Copper thin films: A Structural Exploration**" submitted by **Sabyasachi Panda (108MM016)** and **Sourav Pattanayak (108MM043)** in partial fulfillment of the requirements for the award of **Bachelor of Technology Degree in Metallurgical and Materials Engineering** from National Institute of Technology, Rourkela is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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Abstract

Nucleation and growth mechanism can be classified into mass or diffusion controlled and charge or interfacial controlled. In mass control, the growth is limited by the rate at which the material is transported through the solution to the electrode surface, while in charge control the growth rate is limited by the rapidity with which the ions are incorporated into the new phase. In this project, Cu thin films have been synthesized on graphite substrate using electrodeposition technique which occurs by a process of nucleation and growth. The deposition of Copper thin films on the rough face of the graphite substrate is performed with two different solutions – a mass controlled one (with Na_2SO_4), and a charge controlled one (without Na_2SO_4). The analysis of the corresponding potentiostatic j/t transients suggests a deposition according to 3D instantaneous nucleation. Further, a structural exploration was done into the deposition structure using AFM and SEM technique differentiating the deposition quality via grain based properties.

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Chapter 1: Introduction

1.1. Background

Materials with a very high surface to volume ratio, and a thickness equal to less than 1 μm are called thin films. They behave differently from bulk materials of the same chemical composition. These differences arise out of various factors. They can be smaller size of the crystallites, crystallographic defects such as dislocations, vacancies, stacking faults, grain boundaries and twins which are present in different degrees and orders. In spite of the superior properties of thin films, their reliability is affected by the growth of the films during the service and operation of the device. Grain growth of the films can cause a decrease in hardness, resistivity and the strength of the material. In order to obtain thin films with desired structure and stoichiometry, it is of utmost importance to study their deposition structure, growth and properties in a detailed manner.

In our project we have taken the Electrodeposition technique towards Copper deposition on graphite substrate. Electrochemistry route offers various advantages like low processing temperatures, control of film thickness, easy deposition onto complex shapes, low capital investment and the production of non-equilibrium materials. We have conducted the electrolysis using two different electrolytes – one with Na_2SO_4 , one without it, so as to study the nucleation and growth in different media. We have attempted to study the nucleation and growth behaviour, by electrochemical techniques like cyclic voltammetry and chronoamperometry. Microstructural analysis was done using SEM and structural analysis was carried out using AFM.

1.2. Objectives

The objectives to be achieved in this project are:

- To carry out the in process analysis of the copper deposition on graphite in mass and charge controlled media followed by mathematical modeling using SH model.
- To conduct post synthesis analysis of the copper deposits by SEM and AFM, and compare the structural features.

1.3. Structure of the thesis

This thesis has been divided into 5 chapters. **Chapter 1** constitutes the introduction to the thesis.

In **chapter 2** a brief idea about thin films has been provided with special emphasis on the electrodeposition route of synthesis, nucleation and growth in the two media i.e. charge and mass controlled. The various electrochemical techniques which we have used in our project have also been discussed here.

Chapter 3 contains the experimental details: electrochemical cell arrangement, Atomic Force Microscopy and Scanning Electron Microscopy.

Chapter 4 includes the results of cyclic voltammetry, chronoamperometry and structural analysis techniques to study the structural variations.

Chapter 5 summarizes the results obtained from experiments. A list of references which have been referred for the project has been provided at the end of the thesis.

Chapter 2: Literature Background

2.1. Thin films

When a material has a thickness ranging from fractions of a nanometer to less than one micrometer we call it a thin film. Materials with a thickness greater than a micrometer are classified as coatings. Coatings are mostly used for structural applications like protective covering on cutting tools to improve their wear resistance and hardness. Thin films, however, have both structural and functional applications. They not just improve the endurance of the surface but also improve the overall life of the component. Because of their upgraded optical, electrical, magnetic, chemical and mechanical properties they find use in reflective and anti-reflective coatings, compact discs, sensors, semiconductor devices etc.

The mechanical properties of thin films often differ from those of their bulk counterparts. This is because of the very small size of thin films and the fact that these films are attached to a substrate. Thin films can support very high residual stresses. This residual stress can be relieved later during processing or in the actual device operation through plastic deformation, thin film fracture, or interfacial delamination. The level of the intrinsic stress is comparable with the yield strength of many bulk materials and thus influences the physical and mechanical stability and the properties of the films. The presence of large number of defects and free surfaces hinder the generation and movement of dislocations in a film. This results in the enhancement of the tensile strength of films up to two hundred times the value, in the corresponding bulk material. Flow stresses of thin metal films deposited on rigid substrates are also found to be significantly higher than those observed in the corresponding bulk materials[1].

2.2. Properties and application of thin films

Thin film property-category	Applications
Optical	Reflective/antireflective coatings Interference filters Decoration (color, luster) Compact discs (CDs)
Electrical	Insulation Conduction Semiconductor devices
Magnetic	Memory discs
Chemical	Barriers to diffusion or alloying Protection against oxidation or corrosion Gas/liquid sensors
Mechanical	Tribological (wear-resistant) coatings Hardness Adhesion Micromechanics

In Mechanical properties, the elastic moduli isn't that different from bulk materials. Critical yield strength can be far larger than bulk values[2.3]. It has been shown that the apparently anomalous variations in case of the optical constants of metal films with film thickness can be amounted to the granular nature of the specific films. Even though, not so spectacular variations are observed in dielectric film properties, it is also seen that for certain materials, the optical behaviour does

suggest the presence of marked inhomogeneity as well as anisotropy. Measuring the magnetic properties of the thin film edge further revealed that the magnetic properties of the thin film edge are affected by the thickness of the film and processing conditions during the stripe patterning[4].

2.3. Synthesis of thin films

Synthesis techniques for thin films used in the laboratory are based on physical or chemical vapor deposition. In both the cases, the techniques are based on the formation of vapor of the material to be deposited, so that the vapor is condensed on the substrate surface as a thin film. Usually the process must be performed in vacuum or in controlled atmosphere, to avoid interaction between air and vapor. Other than all these, there are some methods which rely on a mixture of both chemical and physical means. These methods include Molecular Beam Epitaxy, Spin Coating, physical vapour deposition (PVD), chemical vapour deposition (CVD), electrodeposition, Sono-electrodeposition etc. In solid state route and gaseous state route there are some limitations and difficulty in the film formation[5]. These include necessity of high vacuum condition, high temperature condition, complex experimental set-up, requirement of skilled operator etc. These limitations can be overcome by a simple technique. i.e. the electrodeposition.

2.4. Electrodeposition

The process of electrochemical deposition involves the synthesis of solid films from dissolved species by changing their oxidation states using electricity. Pure metals as well as compounds like oxides and phosphides can be easily fabricated by electrochemical deposition. The important applications of this are seen in the electronics industry in the electrodeposition of copper interconnects in integrated circuits and the deposition of thin film magnetic materials, e.g.

CoNiFe alloys. Electrodeposition has also been applied in nanotechnology since it can be used to fill three-dimensional features at room temperature with good control of morphology and thickness. Electrodeposition has various advantages over other processing techniques. It is a cost-effective method for preparation of materials (metals, alloys, compositionally modulated alloys and composites) in the form coatings or as freestanding objects even in complex shapes (foils, wires, electroforms). Also, very low processing temperatures can be attained easily. Low temperature minimizes inter-diffusion or chemical reaction. Deposition can be carried out in a selected specific area and thickness of the deposit can be controlled accurately by monitoring the consumed charge. Deposition rates are seen to be in the order of several tens of microns per hour.

It is a very convenient technique for producing thin multilayered materials. The electrochemical reactions take place at the interface between the electrode and the electrolyte and the driving force of these reactions is the electrical and chemical potentials developed in the electrolyte. What a typical electrode reaction involves is the transfer of charge between an electrode and a species in solution.

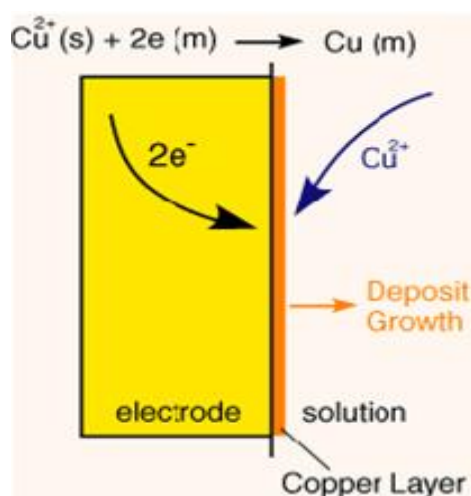


Figure 2.1.: Mechanism of electrodeposition

The electrode reaction usually referred to as electrolysis, normally involves a series of steps:

1. Reactant (O) moves to the interface – this, is termed as mass transport.
2. Electron transfer can then easily occur via quantum mechanical tunneling between the electrode and reactant close to the electrode (typically, tunneling distances are < 2 nm)
3. The product (R) moves away from the electrode in order to allow fresh reactant on to the surface. One of the simplest examples of an electrode reaction is the single electron transfer reaction, e.g. $\text{Cu}^{2+} + \text{e}^- = \text{Cu}$, which has been shown in the figure below.

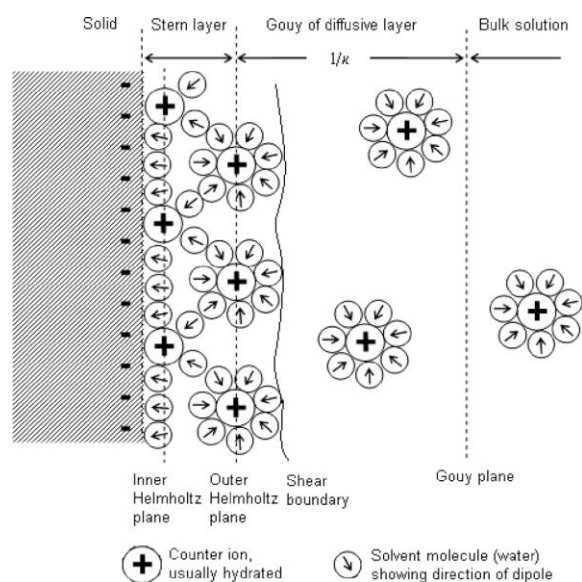


Figure 2.2: The electrical double layer, showing the adsorption of unhydrated ions at the inner Helmholtz plane and of hydrated ions at the outer Helmholtz plane, together with the diffuse layer which extends outwards into the bulk solution.

Electrodeposition occurs in a very thin region in front of the electrode. The ions need to pass through an electrical double layer present on the cathode surface[8]. This double layer acts like a parallel plate condenser with one plate being the metal surface with excess charge, while the other plate, formed by the solvated ions. Most anions give away part of that solvation shell while entering the double layer in order to form a chemical bond with the surface of the electrode. The

bulk solution area is the diffusion controlled area, and is the one we are concerned with. The electrode electrolyte interface region is predominantly charge-controlled.

For the formation of thin films during electrodeposition, nucleation and growth are one of the two major mechanisms. Metal ions are present in a hydrated state in the bulk electrolyte. When a potential is applied, they move towards the cathode owing to the potential gradient. These ions pass through a diffusion layer and an electrical double layer in the process getting stripped off from the hydrated complex becoming bare metal ions. Then the bare metal ions get discharged by combining with electrons on the surface of the cathode thus becoming neutral atoms. These atoms then start migrating over the substrate until they get adsorbed at active sites. Steps and kinks present on the surface act as the active sites for adsorption[9].

At these sites, successive adsorption of atoms occurs resulting in continuous spreading of the mono atomic layer over the substrate surface. Initially, the adsorbed species are not in thermal equilibrium with the substrate and move over the substrate surface. In this process they interact with themselves forming bigger clusters. The clusters are thermodynamically unstable and get desorbed with time. But if the clusters collide with other such adsorbed species before getting desorbed, they start growing in size[10]. Once a certain critical size is reached, the cluster overcomes the nucleation barrier and becomes thermodynamically stable. The critical nuclei grow in number as well as in size until a saturation nucleation density is reached. The next stage is coalescence in which the small nuclei clusters coalesce with each other in order to reduce the surface. This tendency of forming bigger clusters is known as agglomeration and is enhanced by increasing surface mobility of the adsorbed species. When larger islands grow, they leave certain

portions of uncovered substrate in the form of holes and channels which are then filled up later on, forming a continuous film.

Nucleation can be defined as the process in which a new phase is generated from an old phase when its free energy becomes higher than that of the emerging new phase. This transformation from old phase to new phase occurs only when the nuclei overcome a free energy barrier. This can be better understood by considering the free energy changes associated with a nucleus formation.

The molecules present at the surface of the nuclei are less well bound to their neighbours than those molecules which are present at the interior. Hence, their contribution to the free energy of the new phase is greater. The difference between the energies of the surface molecules and those that are present in the bulk is termed as surface free energy. When size of the nucleus is small, there is more number of molecules at the surface and thus the nucleus gets unstable. So, addition of more molecules increases the energy of the system and the nucleus dissolves. Once the nucleus size is large enough, the drop in free energy of the system due to the formation of the bulk phase, is much larger than the surface free energy, thereby resulting in an overall decrease in the free energy of the system.

This intermediate size at which the free energy of the system is decreased irrespective of whether the nucleus grows or dissolves is known as the critical size. Thus, the probability of nucleation is affected by the size of the critical nucleus which is a function of the interfacial energy. The smaller the interfacial energy, smaller is the critical size required for nucleation and thus formation of new phase is relatively easier. Hence, the probability of nucleation can be

manipulated by varying the solution composition or supersaturation. The figure below shows the change in the overall free energy associated with the formation of the new phase.

Growth can be defined as the increase in size of the particle beyond the critical size. The relative rates of nucleation and growth decide the grain size. If nucleation rate is high, large number of grains are obtained. A high nucleation rate combined with a low growth rate results in fine grained structure. Furthermore, nucleation and growth mechanism has also been classified into diffusion (or mass) controlled and interfacial (or charge) controlled. In diffusion control, the growth is limited by the rate at which the material is transported through the solution to the electrode surface while in charge control, the growth rate is limited by the rapidity with which the ions are incorporated into the new phase. While the former is favored by low concentrations and high overpotentials, the latter is favored by high concentrations and low deposition overpotentials.

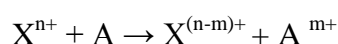
2.5. Mass Transfer

Mass transfer is defined as the movement of material in a solution from one location to another. There are three modes of mass transport in an electrochemical system. They are diffusion, convection, and migration. Diffusion is defined as the movement of material from a higher concentration to a lower concentration in which the concentration. The movement of charged species due to a potential gradient is called Migration. Electrolysis is defined as the movement of electrons with a minimal amount of electro-active species through migration that is carried out due to an excess of inert electrolyte in the solution so that the current of electrons through the external circuit can be balanced by the passage of ions through the solution between the electrodes. Convection is the movement of a material that is carried out by mechanical forces and

usually can be eliminated on a short time scale[11]. In the electrode the rate of reaction can be influenced by the cell potential difference. However, the transport rate to the surface can also effect as well as even dominate the overall reaction rate.

2.6. Charge Transfer

A charge-transfer reaction is defined as the process in which one or more electrons are transferred from one species to another when these two separate species are brought together



The theoretical study of charge-transfer is basically the calculation of the time-dependent behavior of different colliding molecules. These collision processes, unlike isolated and stable molecules, involve very high nuclear speeds.

Rate constants for an electron transfer step vary exponentially to the applied voltage. Therefore a change in applied voltage would mean a change in rate of electrolysis. This exponential relationship is the fundamental basis of voltammetry. However, the overall electrolysis reaction is controlled not only by electrolysis reaction but also by rate of transport to the electrode.

Cyclic voltammetry

Voltammetry is one of the techniques which electrochemists employ to investigate electrolysis mechanisms. There are numerous forms of voltammetry. Cyclic Voltammetry is an electrochemical technique which allows probing the mechanism of transport properties of a system in a solution. In this technique, a three electrode arrangement is used in which the potential relative to a certain reference electrode is scanned at a working electrode, while the

resulting current supposed to be flowing through a counter (or auxiliary) electrode is monitored in a quiescent solution. It makes a quick search of the redox couples present in the system and once those are located, a couple could be characterized by more careful analysis of the cyclic voltammogram[12].

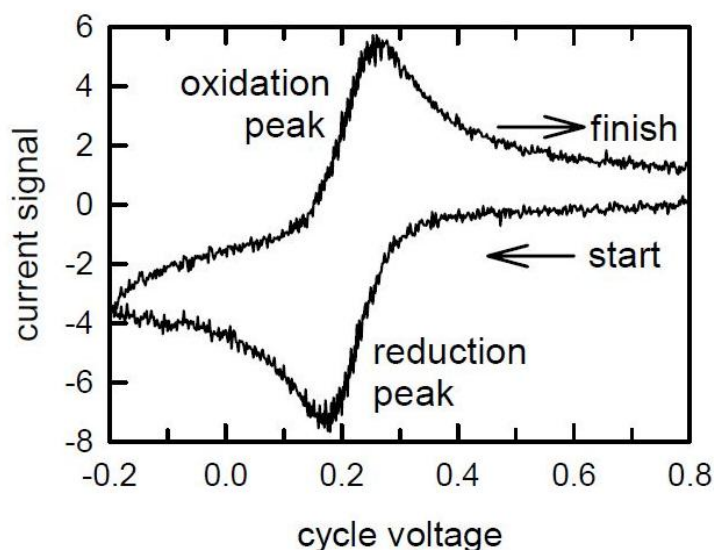


Figure 2.3: Cyclic voltammogram

Normally the potential is scanned back and forth linearly with time between two real extreme values – the switching potentials that use triangular potential waveform. The scan shown in the figure starts at a slightly negative potential, (A) up to some positive switching value, (D) at which the scan is reversed back to its starting potential. The current is first observed to peak at E_{pa} (with value i_{pa}) clearly indicating that an oxidation is taking place. It then drops due to depletion from the diffusion layer, of the reducing species. In the time of the return scan, the processes are reversed (reduction occurring now) and a peak current (corresponding value, i_{pc}), is observed at E_{pc} .

The observed faradic current's magnitude can provide information on the overall rate of those many processes occurring at the surface of the working electrode. Like any other multi-step

process, the overall rate is always determined by the slowest step. Generally, the electrode reaction rate is governed by the rates of processes such as –

- Mass transfer
- Electron transfer at the electrode surface
- Chemical reactions that precede or follow the electron transfer (can be homogeneous or heterogeneous processes)
- Other surface reactions like adsorption, desorption, or crystallization (electrodeposition)

Chronoamperometry

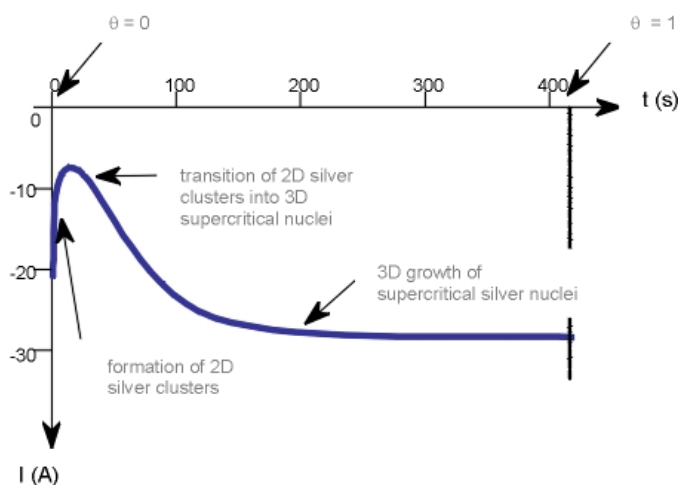


Figure 2.4.: A typical Chronoamperometry

Chronoamperometry (CA) is an electrochemical method in which a step potential is applied and the current, i (A), is measured as a function of time, t (s). This i - t response is comprised of two components: the current owing to the charging of the double-layer and the other due to the electron transfer reaction with the electroactive species. When the working electrode is immersed in the electrolytic solution, a very thin region called the double layer is formed at the electrode-electrolyte interface. The double layer contains a distribution of ions at the interface and is considered to work as a capacitor (C) that represents the electrode double-layer capacitance

[6,7]. The current (i.e., electrons) flows to the working electrode (WE) in order to bring its potential to some desired value. A potentiostat with a 3-electrode cell provides the current via the auxiliary electrode (AE) to the WE while the potential is measured with respect to a reference electrode (RE).

Potentiostatic transients or chronoamperograms are used to evaluate induction times, nucleation rate constants, the mode of nuclei appearance and nuclear number densities. A typical current-time transient for nucleation along with overlapping has been shown in the figure below.

If we see, the current transient shows a falling current section, a rising section and again a falling section corresponding to the double layer charging, nuclei appearance on the substrate and the subsequent growth of electro active area as established nuclei grow. Fleischmann and Thirsk, and Pangarov worked on ‘constant overvoltage’ for studying the nucleation and growth of electrodeposited materials. The current-time transients they recorded did show maxima, which were followed, by approximately exponential decay. This suggested that the nuclei were formed according to the equation

$$dN/dt = AN_0 e^{(-At)}$$

Where, t is the time since the potential was applied, N the number of nuclei, N_0 the saturation nucleus density (number of active sites), A the nucleation rate constant (a potential dependent constant with units of nuclei s^{-1}). This nucleation rate law is of great significance and is assumed

as a basis for one entire family of more sophisticated models that have been developed for the analysis of the process.

2.7. Nucleation and growth analysis

Nucleation and growth is essentially the formation of a continuous, complete, and single layer of atoms. Many experimental observations revealed that there are three basic mechanisms governing the formation of thin films. In general film formation can be the result of any of the following three modes -

1. Frank-Van der Merwe Growth (Layer by Layer Growth),
2. Volmer-Weber Growth (3D Nucleation, Island Growth)
3. Stranski-Krastanov (SK Growth, Mixed mode)

Which mechanism actually dominates in the formation of a multilayer depends on the strength of interaction between the atoms of the growing film and between the atoms of the film and the substrate[13]. Figure 1.1 illustrates these three basic modes of initial nucleation in the film growth. Analysis of the nucleation and growth was carried out using electrochemical techniques like cyclic voltammetry and chronoamperometry further to which, modeling was carried out using the SH model.

Chapter 3: Experimental details

3.1. Experimental Setup:

Electrochemical studies or experiments were conducted with a potentiostat/galvanostat (Eco Chemie Netherland, Autolab PGSTAT 12) system having computer interface of GPES software and a system of three electrode electrochemical cell. Experiments were performed on graphite (Asbury, USA) substrate with exposed surface area of 0.25cm². A platinum rod of 0.2 cm diameter and an Ag/AgCl electrode (Eco Chemie, Netherlands) served as counter and reference electrodes respectively. Chronoamperometry was performed next for the temperature of 25°C mentioned above at potentials of – 0.3 V, – 0.4 V and – 0.5 V. A scanning electron microscope (SEM JEOL 6480 LV) equipped with an energy dispersive X-ray detector of Oxford data reference system were used for the morphological analysis of the copper deposited at different experimental conditions. Atomic force microscopy was done in contact mode with a conducting P(n) doped silicon tip were obtained with a SPMLab programmed Veeco diInnova MultiMode Scanning Probe Microscope.

3.2. Electrolytic Bath Preparation:

The electrolytic bath contains CuSO₄.5H₂O and 98% conc. H₂SO₄, Na₂SO₅. The purpose of using conc. H₂SO₄ is to make the solution electrically conductive. All chemicals were from commercial sources and were of highest purity available. They were used without further purification. Solution was prepared from an additive free copper sulphate bath with doubly distilled water.

3.3. Characterization technique:

Atomic Force Microscopy

Scanning Probe Microscopy (SPM) is that branch of microscopy which forms images of surfaces using a physical probe that actually scans the specimen. An image of the surface is obtained by

mechanical movement of the probe in one raster scan of the specimen, line after line, and recording the probe-surface interaction as one function of position. Scanning probe microscopes can actually image several interactions, and that too simultaneously. The manner or way of using these interactions in order to obtain an image is generally called a mode i.e. AFM, MFM, LFM, EFM, STM, SECM and many more. AFM or scanning force microscopy (SFM) demonstrates resolution of fractions of a nanometer by feeling the surface with a mechanical probe. These images in contact mode with a conducting P(n) doped silicon tip were obtained with a SPMLab programmed Veeco diInnova MultiMode Scanning Probe Microscope. In some other graphs SIEKO SPA 400 atomic force microscope (AFM) with a silicon probe in non-contact mode was also used to take the AFM figures. The scans were taken at scan rates of 1 Hz. Images are taken to analyze the surface's physical properties in micron and sub-micron levels. However, 3D micrographs can be obtained from the analysis.

Scanning Electron Microscope

SEM is a type of microscopy technique that images the sample surface by scanning it with a high-energy beam of electron in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. Microscopic studies to examine the morphology, particle size and microstructure were done by a JEOL 6480 LV SEM equipped with an energy dispersive X-ray detector of Oxford data reference system. Micrographs were taken at accelerating voltages of either 15 or 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.

Chapter 4: Result and Discussion

4.1. Cyclic Voltammetry

Cyclic voltammetry (CV) was performed in the [0.8 to -0.6] V potential range to identify the presence of the electrodeposition processes and to verify the electrochemical behavior of the electrodes in the electrodeposition bath. Figure 4.1. shows typical CVs for brass electrodes obtained with a scan rate of 10 mV/s. Both voltammograms are characterized by the presence of cathodic-anodic peaks associated with deposition and dissolution of Cu. Furthermore, in the two curves, it is possible to note the presence of crossovers of the cathodic and anodic branches, typical of the formation of a new phase, involving a nucleation followed by diffusion limited growth process.

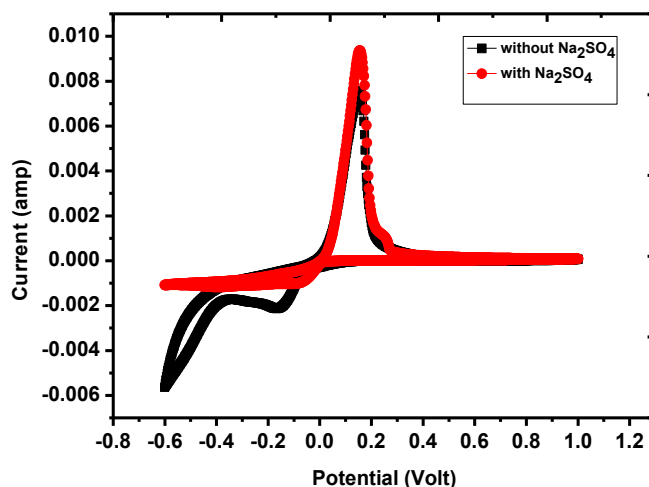


Figure 4.1: Cyclic voltammetry of copper deposition on brass under silent and sonication at a scan rate of 10 mV/s

It is found that with Na₂SO₄ bath the reduction (cathodic) potential decreases i.e. the peak values are shifted towards the positive axis. This may mean that with Na₂SO₄ bath the deposition is feasible at lower potentials. The cathodic peak current (I_c) is directly proportional to the bath

concentration. The main striking feature of the voltammograms is that the plot during the anodic part of the cycle crosses over the plot of the cathodic cycle. This point on the CV where the cathodic and anodic currents intersect is referred to as the crossover voltage. The presence of crossovers indicates the presence of a 3D nucleation. It is also observed from Fig.8. that the current of the reversed scan was always larger than that of the forward scan. This may be because most of the reduced copper was available for dissolution into Cu (II) ions.

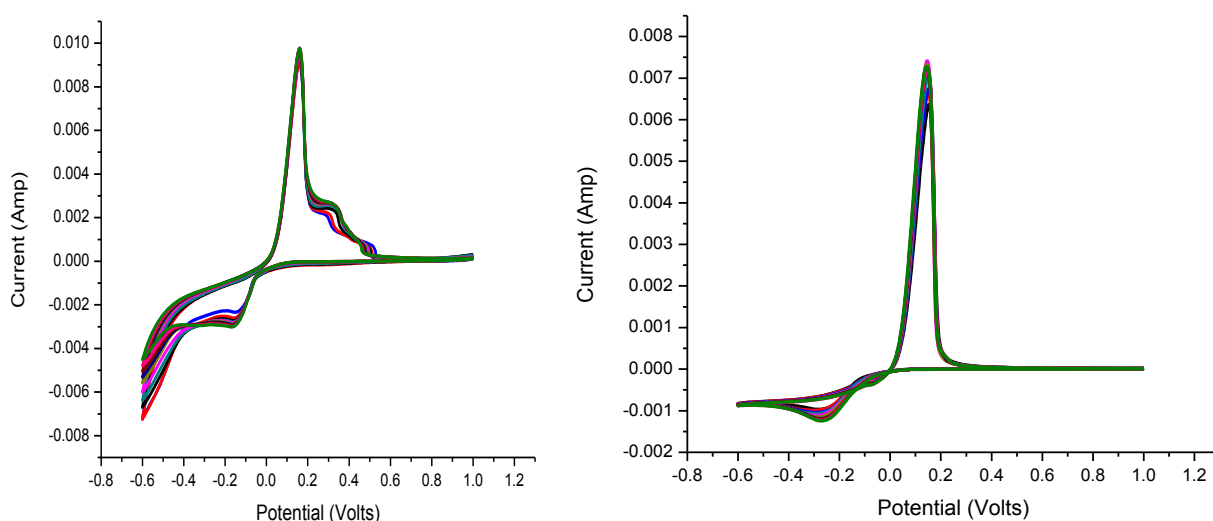


Fig. 4.2: Cyclic voltammograms for a graphite electrode in CuSO₄ bath for (i)with Na₂SO₄ (ii)without Na₂SO₄ at a scan rate of 10 mV s⁻¹. and for 10 cycles.

For more detailed characterization of the nucleation processes, Chronoamperometric analysis was done. Quasi reversible process occurs when $E_{pc} - E_{pa} > 70\text{mV}$ and $I_c/I_a > 1$ (If I_c/I_a is less than 1 then the reaction is a charge controlled reaction and if I_c/I_a is equal to 1 then it is a reversible reaction) With increasing ratio, the process keeps approaching the reversible case. For small values, the system does exhibit an irreversible behaviour. Overall if we see, the voltammograms of a quasi-reversible system are usually more drawn out and exhibit a relatively

larger separation in peak potentials when compared to a reversible system. For reversible nucleation reactions, the efficiency of the process is given by $Q_a/Q_c=1$. If it is less than 1 or greater than 1 then it would mean that there are other anodic or cathodic ions getting discharged respectively. Moreover for a reversible process $E_{pc}-E_{pa} < 70\text{mV}$

Table-4.1: Key features of CV for Cu deposition under silent and insonated conditions

Item	Without Na_2SO_4	With Na_2SO_4
Cathodic deposition peak Current (Amp)	-0.111×10^{-2}	-0.121×10^{-2}
Anodic deposition peak Current (Amp)	0.402×10^{-2}	4.673×10^{-2}
Cathodic deposition peak potential (Volt)	-0.397	-0.365
Anodic deposition potential (volt)	0.211	0.205
Q^+/Q^- (mC)	0.72	0.78

4.2. Chronoamperometry

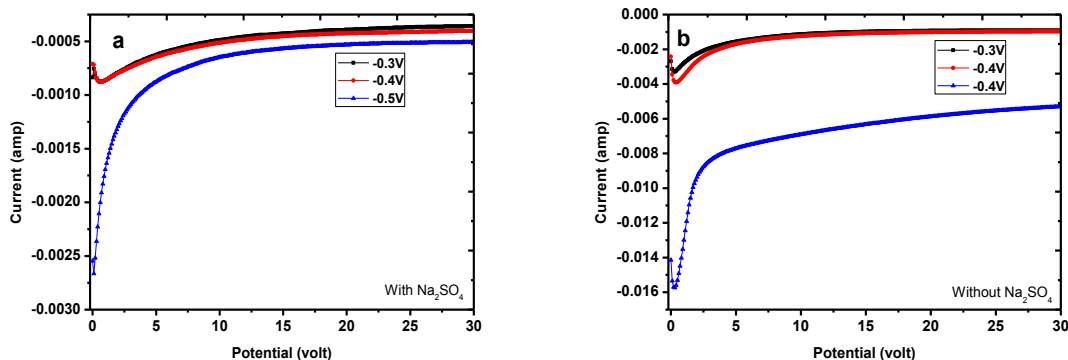


Figure 4.2: Chronoamperometry of Copper (a) with and (b) without Na₂SO₄

Figure 4.2 (a-b) shows the series of current transients (CT) for copper deposition with and without Na₂SO₄. The varying deposition overpotential effect is shown in all figure. From fig. it can be clearly seen that the shape of the current transients changes as the deposition potential is change. At high deposition potential, the transients exhibit a sharp drop in current density followed by shallow current densities which have been assigned to adsorption and diffusion controlled growth processes respectively in both the bath. Such an observation is in agreement with deposition studies observed by following this rising section of transient, a period of slow current decay occurs. It is also clearly visible that the current decay after rising portion does not decay fully, approaching a value of zero. One possible explanation for this could arise from the fact that hydrogen could have evolutes and, therefore, the value of current density after a sufficiently long period is due in part of the evolution of hydrogen.

The theoretical formulations utilized for the description of the phase formation onto a substrate usually consider two extreme cases of nucleation: instantaneous and progressive. In instantaneous nucleation all nuclei form at the same time and grow comparatively slowly. In

progressive nucleation new nuclei form during the course of deposition process and grow relatively faster [31]. In this paper we use theoretical non-dimensional curves of these extreme cases of nucleation for 2D or 3D growth. It helps us to define the dominant mechanism of the nucleation and growth for each of the studied temperature. The current transients obtained above are represented in dimensionless form and compared with theoretical transients. The equations are usually used in the form of dimensionless curves, in which either (I/I_m) or $(I/I_m)^2$ is plotted against (t/t_m) , with I_m and t_m being the current maximum of the measured potentiostatic transient, and the corresponding time, respectively. Of the methods of potential use in the interpretation of current transients with well defined points of maxima, we decided to use the model developed by Bewick et al. and Sharifker and Hills for the analysis of 2D and 3D nucleation mechanism and kinetics respectively. Equation (1) and (2) are used to plot the theoretical model for 2D instantaneous and progressive nucleation respectively.

$$\frac{I}{I_m} = \frac{t}{t_m} \exp \left[\frac{1}{2} \left\{ 1 - \left(\frac{t}{t_m} \right)^2 \right\} \right] \quad (1)$$

$$\frac{I}{I_m} = \left(\frac{t}{t_m} \right)^2 \exp \left[\frac{2}{3} \left\{ 1 - \left(\frac{t}{t_m} \right)^3 \right\} \right] \quad (2)$$

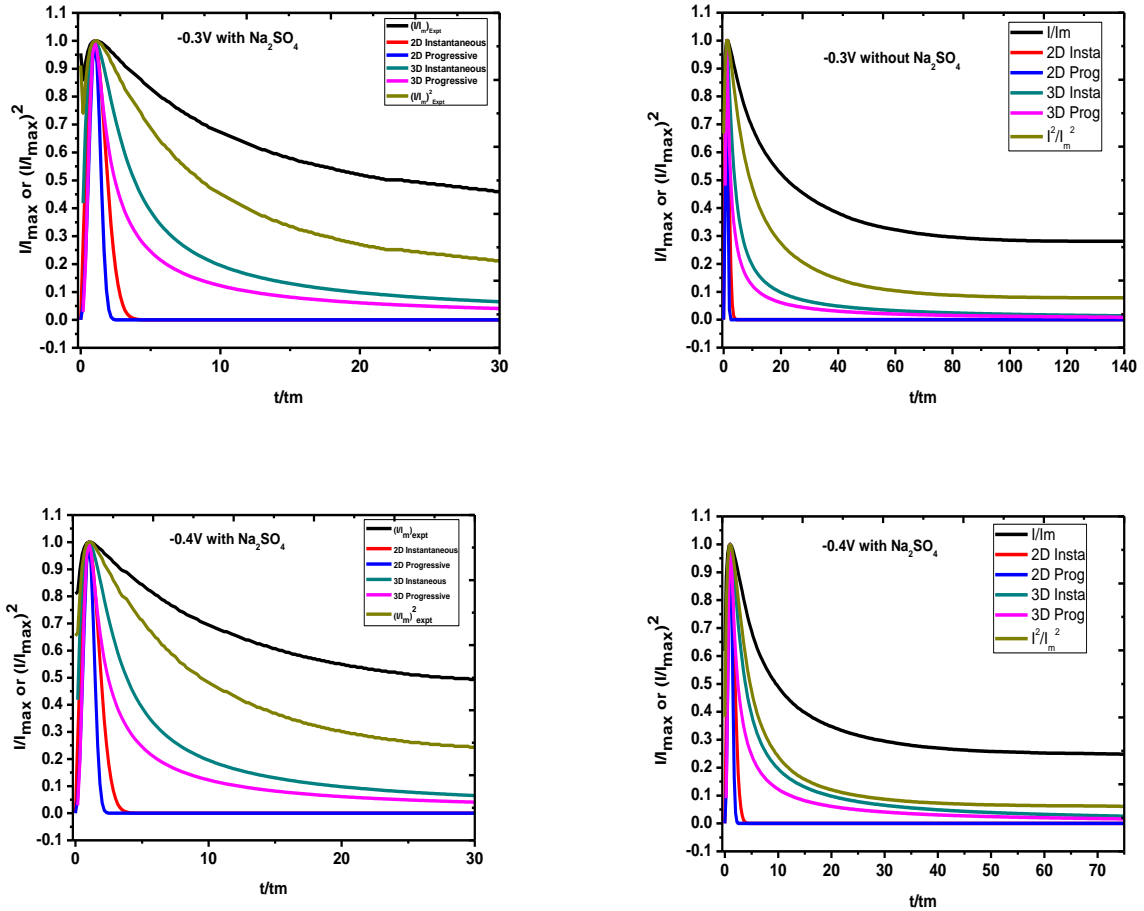
Equation (3) and (4) are used to plot the theoretical model for 3D instantaneous and progressive nucleation respectively [15].

$$\frac{I^2}{I_m^2} = \frac{1.9542}{\frac{t}{t_m}} \left\{ 1 - \exp \left[-1.2564 \left(\frac{t}{t_m} \right) \right] \right\}^2 \quad (3)$$

$$\frac{I^2}{I_m^2} = \frac{1.2254}{\frac{t}{t_m}} \left\{ 1 - \exp \left[-2.3367 \left(\frac{t^2}{t_m^2} \right) \right] \right\}^2 \quad (4)$$

At more negative potentials, there is pronounce current decay that is typical of planar diffusion-controlled growth. However, the current does not decrease as fast as predicted by the Cottrell

equation, indicating mixed diffusion/kinetic control. Furthermore, the figure shows that, for longer time (t / t_m), the experimental data are in good agreement with the grow law for instantaneous nucleation followed by diffusion limited growth with obvious positive deviation from the theoretical plot. This deviation can be attributed reasonably to the presence of a parallel reaction to the Cu film electrodeposition process. Table 4.2 shows the calculated diffusion coefficient D and nucleation number density N (according to Eqs. [5] and [6]) for the Cu depositions in both the bath.



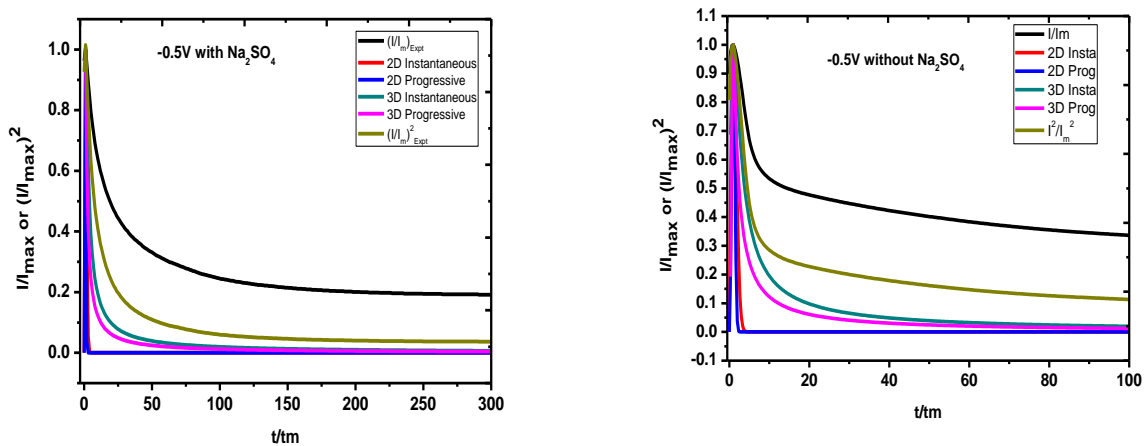


Figure 4.3: $(I/I_{\max})^2$ or (I/I_{\max}) vs. (t/t_{\max}) analysis of Chronoamperometry for Cu with the data for the theoretical instantaneous and progressive nucleation modes for varying deposition potentials

$$D = \frac{t_m I_m^2}{0.1629 z F C^2} \quad (5)$$

$$N = \frac{1.2564}{t_m \pi K D} \quad (6)$$

where z is the number of electrons involved (in these equations, the number of electron involved are 2), F is Faraday's constant of 96,500 coulomb, C is bulk concentration of the electrolyte and k is a constant, where q is the density of copper (8.9 gm/cc) and M is the molecular weight of Copper.

Table 4.2.: Characteristic Kinetics Parameters of $i(t)$ transients obtained for sonicated Cu deposits for different deposition potential

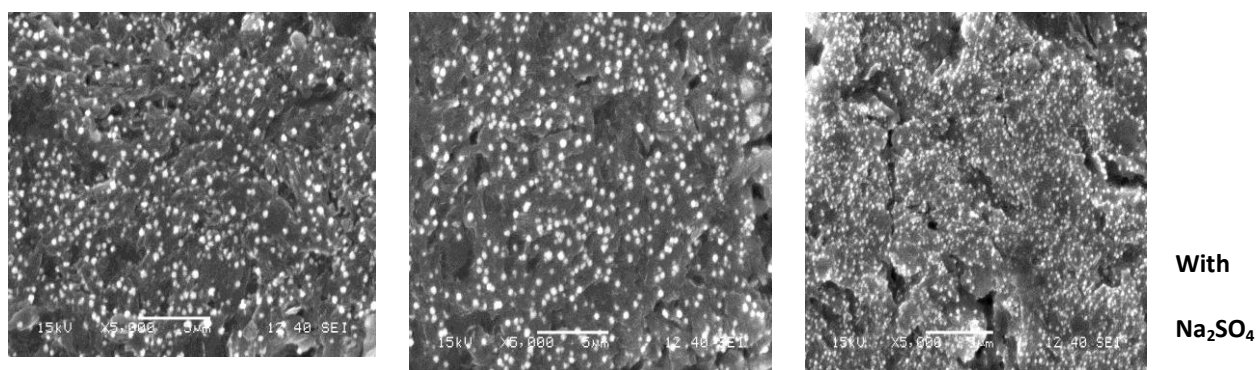
Deposition potential (V)	I_{\max} (A/cm ²)		t_{\max} (sec)		Nucleation density (x10 ⁸)		Charge (mC)	
	With Na ₂ SO ₄	Without Na ₂ SO ₄	With Na ₂ SO ₄	Without Na ₂ SO ₄	With Na ₂ SO ₄	Without Na ₂ SO ₄	With Na ₂ SO ₄	Without Na ₂ SO ₄

-0.4	-8.7E-4	-3.9E-3	0.6	0.4	2.16	3.744	-15.4	-40.9
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4.3. Microstructural characterization

4.3.1. Scanning Electron Microscope:

Fig. 4.4 shows the SEM micrographs for the films deposited at different deposition potentials with and without Na_2SO_4 . It was found that bath concentration and deposition potential strongly affects the density and morphology of Cu nuclei, their size and the surface coverage. The images display that there is good surface coverage at higher deposition potential. Sodium sulfate bath is having finer grain size. This may be due to the diffusion control system restrict the particles to grow. It helps in increasing the rather the nucleation rate. At higher deposition potential we confirmed from Chronoamperometry that, the charge consumed is high and current density is also high. So there is driving force to nucleate the particles is more and growth rate is less, so that the finer grain can be obtained.



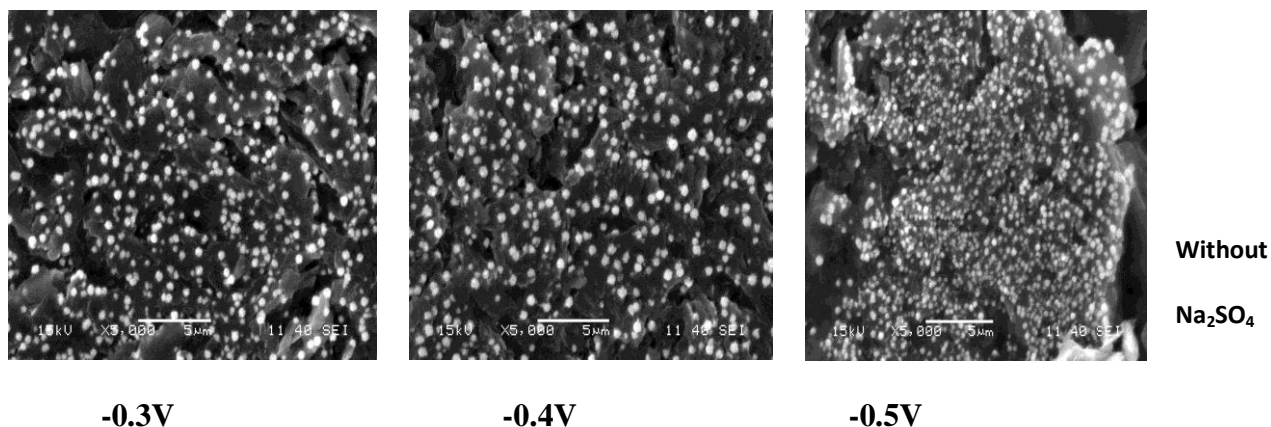
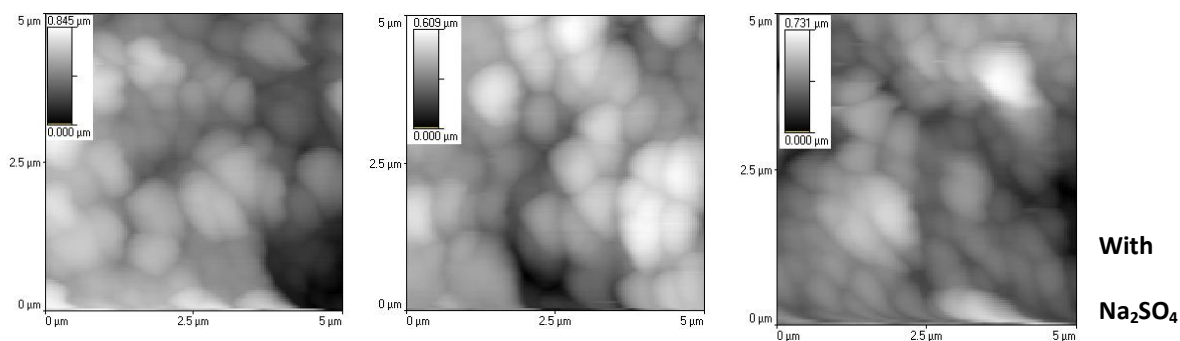


Figure 4.4: SEM Micrographs of Copper with and without Na₂SO₄ at different deposition potentials

4.3.2. Atomic Force Microscope

Figure 4.5. shows the SEM micrographs for the films deposited at different deposition potentials with and without Na₂SO₄. An increase in uniformity and smoothness of the surfaces morphology with deposition potential and with additive can be clearly observed.



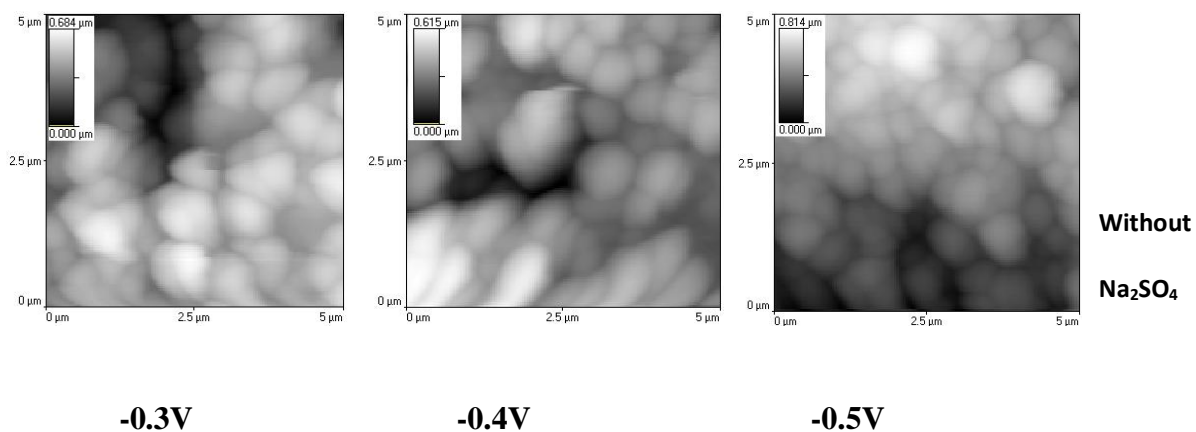


Figure 4.5: AFM Micrographs of Copper with and without Na_2SO_4 at different deposition potentials

The grains appear to be spherical and somewhere agglomerated. The maximum grains of deposit are in the size range of 400-600 nm with a maximum height of 376 nm and average roughness of 300 nm. The complete analyses of the deposits are given in Table 4.3.

Table 4.3.: Roughness and grain size by AFM analysis

Potential (V)	Roughness (nm)		Grain size (nm)		Thickness (nm) measured	
	With Na_2SO_4	Without Na_2SO_4	With Na_2SO_4	Without Na_2SO_4	With Na_2SO_4	Without Na_2SO_4
-0.3	182.6	163.8	258	323	227.27	210.69
-0.4	124.0	211.6	355	420	330.14	311.34
-0.5	217.9	145.0	387	291	351.8	315.69

Chapter 5: Conclusions

- There is distinction in between the two modes of experimented conditions.
- The deposition follows 3D instantaneous nucleation route irrespective of mode of deposition
- Surface structures are superior in case of charge transfer mode of discharge of Cu ions
- However the nature of the substrate has a definite role and has to be addressed properly before drawing a critical conclusion.

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