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UNIVERSITY OF CALIFORNIA, SAN DIEGO

Nanograin Copper Deposition Using an Impinging Jet Electrode

A Thesis submitted in partial satisfaction of the
requirements of the degree of Master of Science

in

Chemical Engineering

by

Karen Diane Swingle

Committee in Charge:

Professor Jan Talbot, Chair
Professor Richard Herz
Professor Justin Opatkiewicz

2013

The Thesis of Karen Diane Swingle is approved and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2013

DEDICATION

This thesis is dedicated to my parents, Alan and Ivy, my sister Erica and husband Andy. Without their support this wouldn't have happened.

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ABSTRACT OF THE THESIS

Nanograin Copper Deposition Using an Impinging Jet Electrode

by

Karen Diane Swingle

Master of Science in Chemical Engineering

University of California, San Diego, 2013

Professor Jan Talbot, Chair

Nanograin copper has applications as an interconnect material for microelectronics, telescope mirrors and semi-mirrors for UV filters. Electrodeposition is the preferred method for obtaining nanograin copper due to its low cost and current

use in industry. Impinging jet electrode (IJE) plating systems have plating rates that can be up to 10 times faster than conventional methods.

In this research the use of a circular, unsubmerged IJE for creating copper films on platinum and nickel substrates was investigated. Specifically, the limits of the process parameters for the IJE system of flow rate (2.5 or 7 L/min) and current density (10 or 200 mA/cm²). Also, the process of self-annealing, grain growth at room temperature, of the copper deposits was investigated.

It was found that copper films could be electrodeposited with average grain sizes of approximately 40 nm. Smaller grain sizes were associated with a low flow rate, while a higher flow rate gave larger grains. Grain size did not vary with current density. Self-annealing was observed for deposits made with a high flow rate and grain growth occurred for at least a month. After 8 months only the deposits made using a low flow rate still had grains under 100 nm in size.

1. Introduction

Nanograin materials often show different properties than the material in bulk form. Therefore, there is research focused on nanomaterials and whether they can improve various technologies with these different properties. In the semiconductor industry there is a constant need to find new materials and techniques to decrease the size of integrated circuits. One material that is being investigated to help miniaturize electronics is nanograin copper.¹ Copper is already used extensively in semiconductor processes and the superior strength, electrical and thermal conductivities, wear rate and hardness of nanograin copper makes it an ideal material for electronics.² Specifically, nanograin copper is researched as a interconnect material for integrated circuits, telescope mirror layers and semi-mirrors for UV radiation filters.³

Nanograin copper can be made in a variety of ways, including chemical vapor deposition (CVD), sputtering, and electrodeposition.⁴ Electrodeposition is a favored method for making nanograin copper deposits because it can be done at room temperature and pressure, the properties of the deposit can be tailored by the deposition parameters, and plating can be done on complex shapes.⁵ Another advantage of electrodeposition is that it is already in use in industry to make electronics. There are a variety of electrode configurations used in electroplating. These include parallel plate electrode (PPE), rotating disk electrode (RDE) and rotating cylinder electrode (RCE). The PPE system is the most commonly used system do to its simplicity, but it is difficult to control the hydrodynamics, which can be done easily for the RCE and RDE cells.⁴

The impinging jet electrode (IJE) system is another configuration that allows for good control of hydrodynamics while promoting high rates of mass transfer. The IJE system works by applying an electric field through a jet of electroplating solution flowing through a nozzle, that also acts as the anode, and impinges upon the cathode where selective plating occurs.⁴ To plate large areas an array of jets is used.

IJE's show electroplating rates about 10 times higher than conventional plating methods (typically 10-50 mA/cm²) with current densities up to 4 A/cm².⁴ Copper, nickel and gold have been successfully deposited using an IJE system. Process parameters that affect deposition include flow rate, current density, plating bath composition, distance between the nozzle and cathode and type of substrate.⁴

This research extends the work of Dr. Steve Osborne, who designed, built and tested the IJE system used for this work.⁶ Osborne found deposits with average grain size of 175 nm but with many grains smaller than 100 nm when alumina particles were codeposited.⁶ While running experiments on the use of the IJE system for electrocodeposition of 50 nm alumina in copper, Thiemiig found pure nanograin copper deposits with average grain sizes of 79 and 68 nm.⁷ As his research was a study of electrocodeposition, no systematic study of the parameters that would produce nanograin copper deposits has been done.

The purpose of this work was to determine if indeed nanograin copper deposits could be made with an impinging jet electrode system and the effect of process variables at the limits of the IJE system on the grain size and morphology of the deposits. Since nanograin copper has been known to grow at room temperature, a

process called self-annealing,^{8,9} another goal was measure the grain size of the deposits over time. The process variables that were investigated were type of substrate (platinum or nickel), current density of 10 or 200 mA/cm² and flow rate of 2.5 or 7 L/min.

In the next chapter the process variables of copper electroplating and the properties of nanograin copper will be discussed. In Chapter 3 the impinging jet electrode system will be discussed. Chapter 4 reports the experimental procedure, while Chapter 5 presents the results and discussion. Finally, there are the conclusions and suggestions for future work in Chapters 6 and 7.

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2. Technical Background

Electroplating is a widely-used method for depositing metals onto substrates. Some advantages of electroplating versus other deposition methods, such as chemical vapor deposition (CVD), are faster deposition time, smaller grain sizes (less than 100 nm vs. approximately 120 nm), room temperature and atmospheric pressure conditions, and ability to coat non-planar surfaces.^{1,2} Recently, electroplating has become a viable method for depositing nanograin structures.³ In particular, nanograin copper is being considered for a variety of applications mostly in the electronics field, including interconnections for microelectronics, semi-mirrors for UV radiation filters and telescope mirror layers.⁴

2.1 Copper Electroplating

Copper is one of the most widely deposited metals in the world and it has been electroplated since at least 1810.¹ Electroplated copper has many uses, including plating on plastics, plating on bumpers, zinc die castings, printed circuit boards, cookware and many others.¹ Copper can be used for these different uses because it has a wide range of physical properties, including strength, electrical resistivity, and hardness that can be tailored by the deposition conditions. The main factors in electroplating that affect the copper properties are bath composition, temperature, current density, addition agents and impurities.

2.1.1 Bath Composition

Copper can be deposited from different types of plating solutions including pyrophosphate, alkaline cyanide, fluoborate and acid sulfate baths.¹ Acid sulfate baths are the most popular for commercial use and are used for electroforming, electrorefining and electroplating. The popularity of acid sulfate baths is due to lower cost, ease of control and less susceptibility to impurities.¹ Acid sulfate solutions are used widely to make electrical wires, printed circuit boards, and interconnects for semiconductors.¹ Since electroplating in this research was done using an acid sulfate bath, the effects of other variables will be discussed with reference to an acid sulfate bath.

2.1.2 Temperature

Most electrodepositions are made at room temperature because it is economical to maintain, but electrodeposits are made at temperatures from 18 °C to 60 °C. Higher temperatures result in higher conductivities and thus, reduced activation polarization, when the electrode potential deviates from the equilibrium potential value, for both anode and cathode during electrodeposition.¹

2.1.3 Current Density

Higher current densities typically yield faster deposition with smaller grain sized coatings.¹ At high current densities there is more nucleation than grain growth

during electrodeposition, giving smaller grains, while the opposite occurs at lower current densities.⁵ However, a higher current must be balanced by adequate agitation of the electrolyte to obtain deposits that are pure and adhere well to the substrate. Agitation of the bath is needed because at high current density the deposition becomes mass transport limited and agitation increases the concentration of metallic (copper) ions near the cathode. If the concentration of copper ions is low at the cathode, concentration polarization (mass transport limitation) at the cathode rises, so that other species may be deposited leading to a spongy or powdery deposit with occluded salts.¹

How the current is applied also has an effect on the final deposit. Direct current (DC) plating, which is the norm, is done with a constant current density and generally gives micrograined deposits with grain sizes about 1-2 μm .¹ Deposits made at current densities of 50-60 mA/cm^2 have produced grains as small as 100 nm.⁶

Other types of plating include pulse plating and reverse pulse plating that are used to produce nanograin structures. Pulse plating is where the current is applied periodically with a rectangular waveform as shown in Figure 2.1.^{7,8} Relative to direct current plating pulse plating give smaller grain sizes and a more homogenous surface because higher peak current densities can be used while maintaining a lower average current density to prevent powdery deposits.⁷ Work by Natter and Hemplmann shown in Table 2.1 shows how by changing the time the current is off (t_{off}) and peak current density (I_p) while maintaining the same average current density (I_a) gave grain sizes which varied from 10 nm to 83 nm.⁷

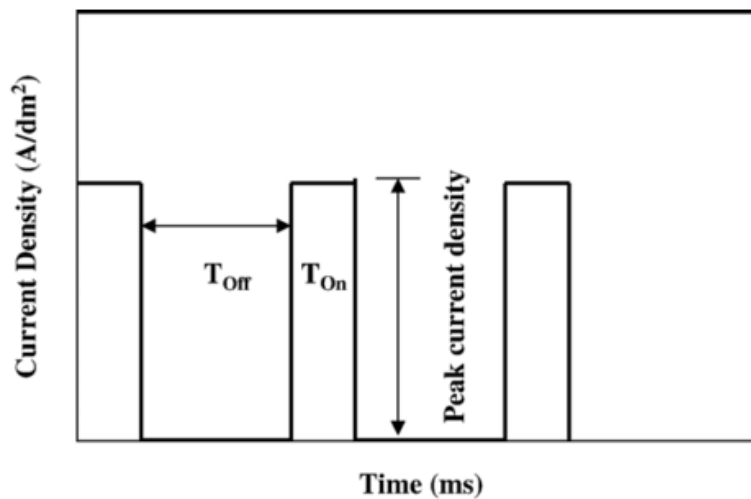


Figure 2.1: Waveform of pulse plating.⁸

Table 2.1: Experimental data for pulse electroplating with different t_{off} times.⁷

Pulse Parameters				
t_{off} [ms]	t_{on} [ms]	I_{pulse} [mA/cm ²]	I_a [mA/cm ²]	grain size $\langle D \rangle_v$ [nm]
100	1	1250	12	10
50	1	625	12	14
25	1	312	12	25
18	1	225	12	32
12	1	156	12	51
6	1	78	12	83

Reverse pulse plating is similar to pulse plating in that the current is only on periodically, but there is also a step where the potential is made anodic and material is removed rather than plated.⁹ Reverse pulse plating is used to obtain smoother deposits and aids in the filling ability of a deposit in a recess.⁹ Figure 2.2 shows a potential density waveform used for reverse pulse plating. Experiments have shown average grain sizes of 100 to 130 nm for reverse pulse plating from average current densities of

4.5 and 3.3 mA/cm² respectively.⁹ In DC and pulse plating there is no control over the fluid flow. The fluid is either stationary or being stirred with a mechanical stirrer.

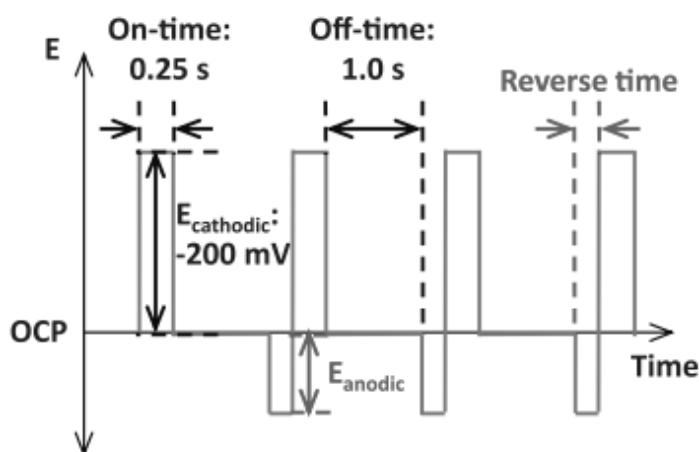


Figure 2.2: Example of a waveform for reverse pulse plating.⁹

2.1.4 Additives

Additives are added to plating solutions to increase brightness, throwing power (the ability of an electroplating solution to give uniform deposits on irregular shaped cathodes), hardness, grain refinement, surface smoothing, and limiting current density (the highest current density that can be used before other ions start to be discharged simultaneously). Nyder included an extensive list of additives in his work and there are many proprietary blends that can be purchased commercially.¹ Typically additives for acid copper plating include thiourea, thiocarbonates, or disulfides to increase brightness, polyoxyalkylene glycols and high-molecular-weight polyether compounds

to smooth the surface, and chloride which acts synergistically with the other additives to increase brightness and leveling.¹

2.1.5 Impurities

Compared to other plating solutions, copper sulfate solutions are more tolerant of impurities.¹ Impurities can be present from other processing steps or can be present from the dissolution or reaction of the anode. Some metallic ions, such as iron and nickel, are only codeposited in very small amounts and end up accumulating in the plating solution reducing the conductivity.¹ Other ions, such as arsenic and antimony, can be codeposited and cause embrittlement and rougher surfaces for the deposits. There are additives and other techniques that can be used to eliminate or mitigate the effect of various impurities depending on the process being used.¹

2.1.6 Substrate

The structure of a deposit can be influenced by the structure of the substrate it is on.¹ This has been seen with substrates that have been cleaned and dipped in acid, but not in substrates that were not dipped in acid. There also is a relation between grain size of the substrate and grain size of the deposit.¹ The influence of the substrate on the deposition lessens as the thickness of the deposit increases as shown in Figure 2.3.¹⁰

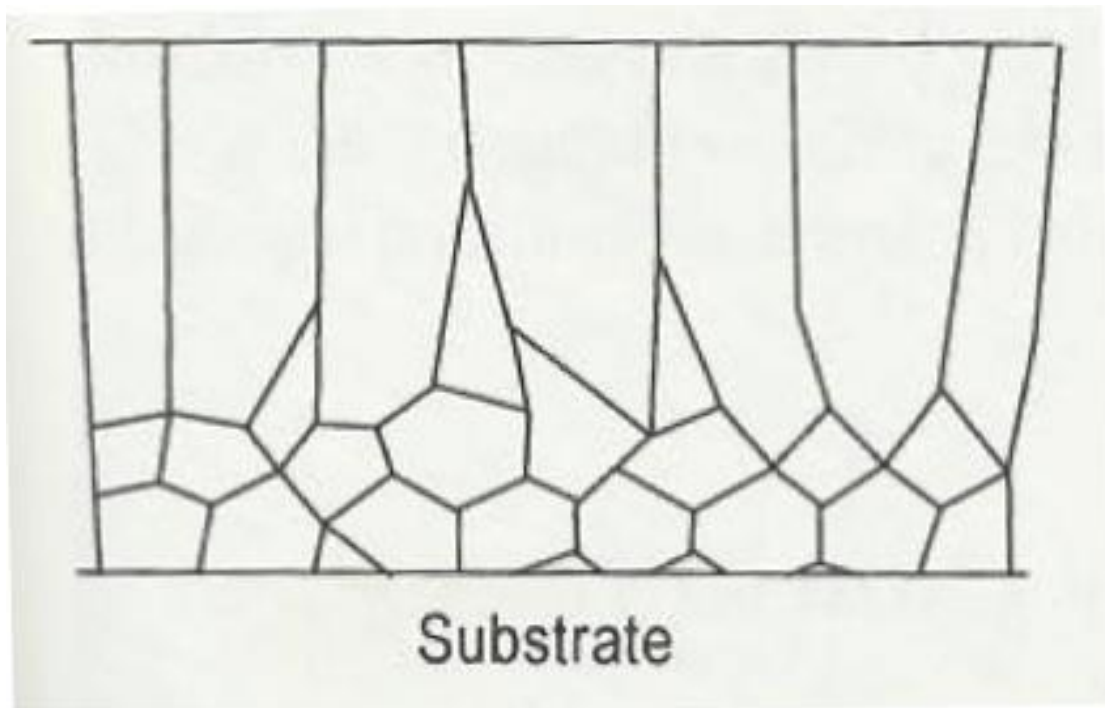


Figure 2.3: Illustration of grain growth perpendicular to the substrate.¹⁰

2.1.7 Morphology

The morphology of copper deposits varies depending on plating conditions. The most common surface morphologies, shown in Figure 2.4, are ridged or ribbed, platelet, block or cuboidal and polycrystalline .¹⁰

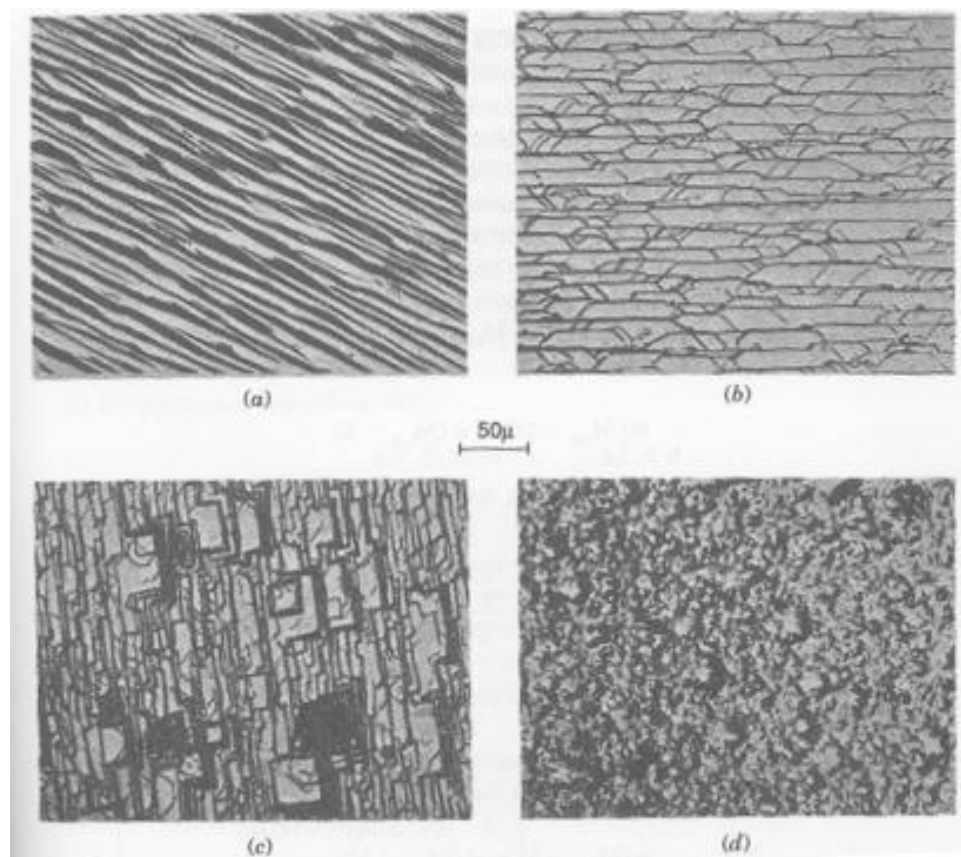


Figure 2.4: The four basic deposit structural forms of Cu deposited from acid copper solutions: (a) ridge, (b) platelet, (c) block and (d) polycrystalline.¹⁰

Other growth forms that are seen are pyramids, polygons and elongated crystals.¹¹ Pyramidal shapes are seen at low current densities with low impurities. As the current density is increased, cuboidal and polygonal shapes are observed.¹¹ At high current densities, which are associated with large overpotentials, the difference between the potential used and the equilibrium potential, deposits can show dendrites and cauliflower-like forms as seen in Figure 2.5.¹² Figure 2.6 shows the evolution of different morphologies as a function of current density normalized to the limiting (maximum) current density.

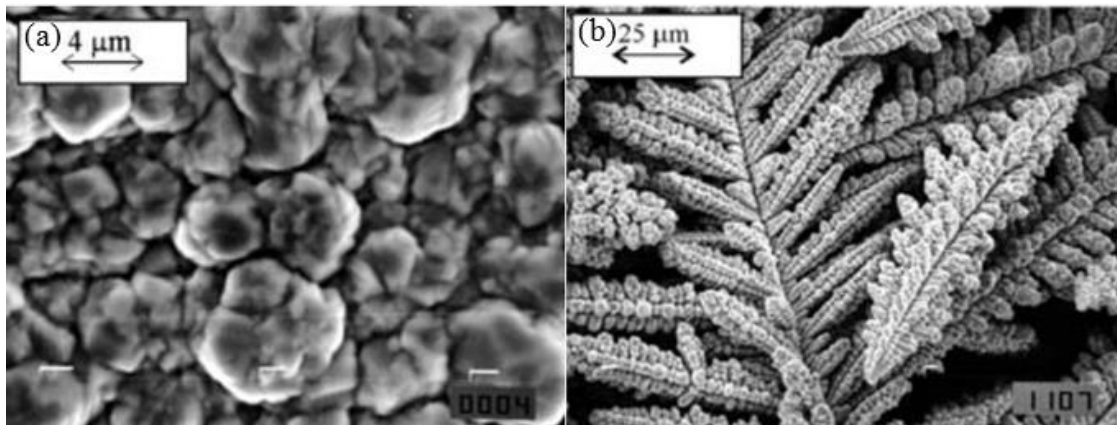


Figure 2.5: SEM image of (a) cauliflower type and (b) dendritic copper deposits.¹²

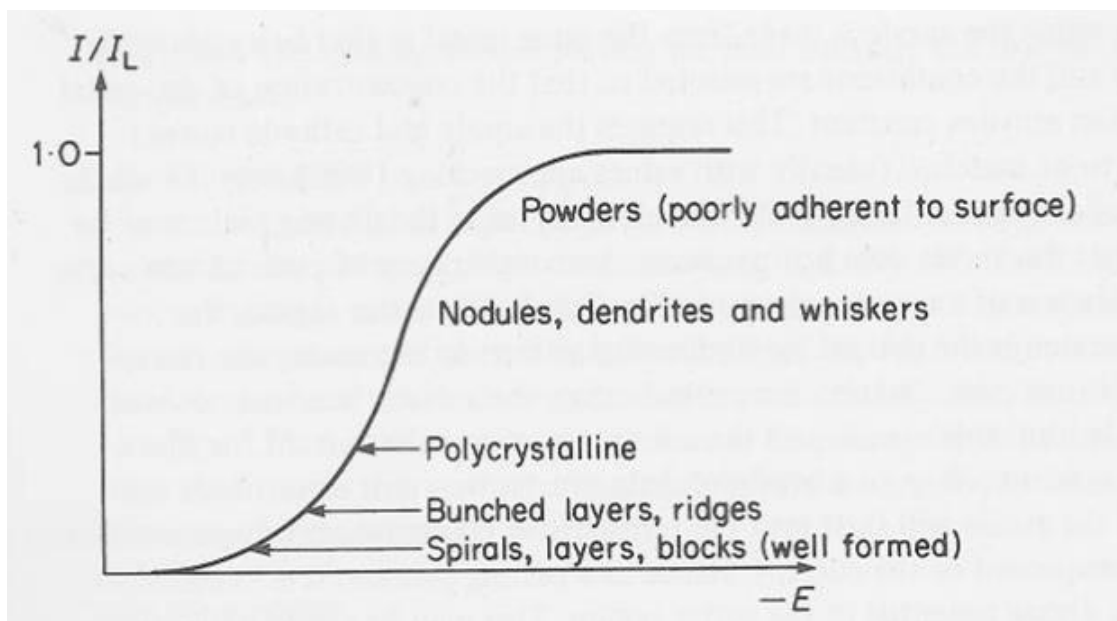


Figure 2.6: The variation of the characteristic growth modes on the current density normalized by the limiting current density.¹³

While the morphology of nanograin copper deposits is not well documented, there is some evidence that the nanograin morphology is very similar to micrograin morphology, just with smaller grains. An example of this is shown in Figure 2.7, which compares the morphologies of a DC-plated deposit with average grain size $2\text{ }\mu\text{m}$ to a pulse plated sample with average grain size 56 nm .¹⁴

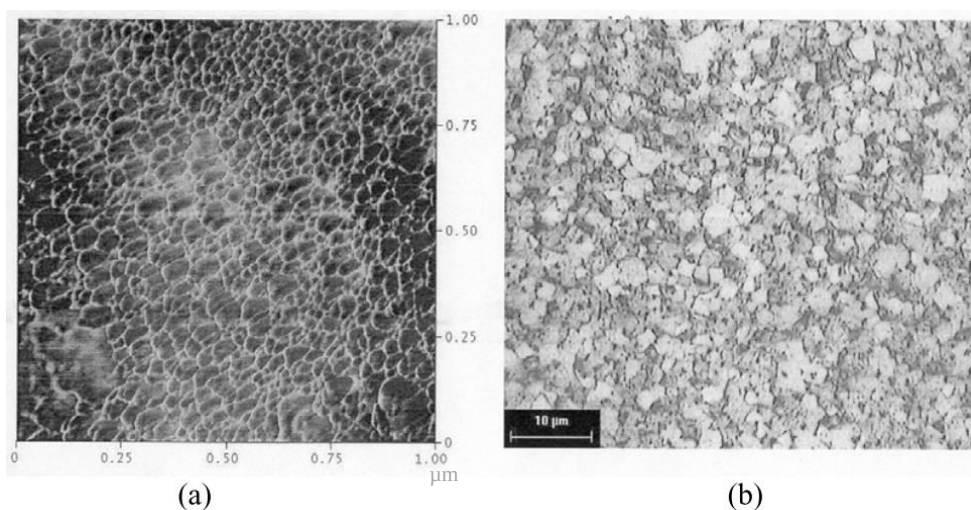


Figure 2.7: (a) A nanocrystalline Cu electrodeposit (56 nm) and (b) a microcrystalline Cu electrodeposit ($2\text{ }\mu\text{m}$).¹⁴

2.2 Nanograin Copper

The characteristics that make copper so attractive for electrical applications are high thermal and electrical conductivities and good mechanical properties. Also, the infrastructure for electroplating copper is already in place in industry, so integration with back end processes, the final steps in making electronic chips, is relatively easy.¹⁵ However, one of the major problems with some nanograin metals, including copper, is grain growth or self-annealing at room temperature.¹⁶

2.2.1 Properties

Nanograin copper exhibits different tribiological, mechanical, electrochemical, and electrical properties than micrograin copper. In most cases the properties of the nanograined deposits are superior to the properties of the micrograin deposits.

2.2.1.1 Hardness

Tao found that the indentation hardness of electrodeposited copper is almost five times higher at about 5 GPa for a 56 nm grain copper deposit compared with a sample with a grain size of 2 μm .¹⁷ This hardening can be attributed to an increase in grain boundaries which retards the movements of dislocations, thus increasing the metals resistance to plastic deformation.¹⁸ For grain sizes of 10 nm or less, the hardness decreases with further grain refinement. The hypothesis for this behavior is that at these sizes the dominant mechanism for deformation is grain boundary sliding or Coble creeping.¹⁸

2.2.1.2 Reactivity

Nanocrystalline copper forms a more stable protective oxide passivation layer than microcrystalline copper, which makes it less reactive.¹⁷ Diffusion on the surface of the deposit is the controlling parameter in the creation of a protective oxide layer and the extra grain boundaries in nanograin copper lead to an increase in diffusion of atoms, vacancies and dislocations.¹⁷ This increase in lattice diffusion is attributed to

the high degree of mass transport along grain boundaries. The protective layer also adheres better to the nanograin copper due to the enhanced electrochemical reactivity at the grain boundaries.¹⁷

2.2.1.3 Friction

Using microscratch experiments Tao¹⁷ found that nanograin copper deposits have a smaller coefficient of friction than micrograin deposits as shown in Figure 2.8. This finding is more prominent at higher applied loads. The explanation for this behavior is that nanocrystalline deposits are harder than micrograin ones and this higher resistance to penetration reduces the ploughing effect and the contact area and thus, reduces friction.

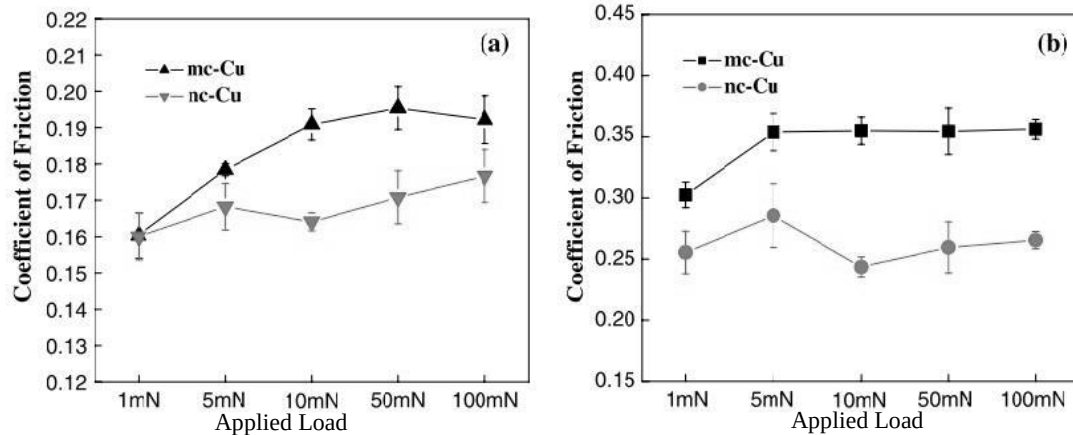


Figure 2.8: Coefficient of friction of nc-Cu (56 nm) and mc-Cu (2 μm) deposits, determined during microscratch experiments using (a) ball tip and (b) a sharp tip.¹⁷

However, different results were found for nanoscratch experiments at light loads, due to different main contributors to friction at different loadings. With high loadings as with the microscratch experiments, the materials hardness dominates friction. For very light loads, such with the nanoscratch experiments, the attractive forces between atoms, like Van der Waals forces, and covalent, ionic and metallic bonds dominate in determining friction. For loads of 100 μN the micro and nano-deposits had similar coefficients of friction (COFs) of approximately 1.5, but at the higher loads of 300 and 500 μN the microdeposits had a smaller COF than the nano deposits, 2 vs 2.5 and 2.5 vs 3, respectively. This is attributed to how well the light loads penetrate the oxide passivation layer that forms on the deposit. The passivation layer which is more than a few nanometers thick but less than 25 nm thick is not breached on either type of sample with 100 μN of force, so the COF is similar. However, with the 300 and 500 μN loads the tip does penetrate the passivation layer leading to the difference in COF being determined by attractive forces between atoms. The nanograin deposits are more electrochemically active under the passivation layer due to the prevalence of grain boundaries and thus, a stronger van der Waals force is present which leads to a higher COF.¹⁷

2.2.1.4 Wear Rate

Micrograin copper is more susceptible to local wear than nanograin copper. In nanowear experiments done by Tao¹⁷ it was found that at loads of 50 μN and 100 μN ,

the nanocrystalline copper showed less wear than the micrograin copper as shown in Figure 2.9. Even though the COF of the materials under these small loads was the same, the differences in wear stems from wear dependence on local structure, roughness, and the thickness and adhesion of the oxide film. The nanocrystalline copper has a higher grain boundary density that leads to it having a stronger and more adhesive oxide layer, thus giving it a higher resistance to local wear.¹⁷

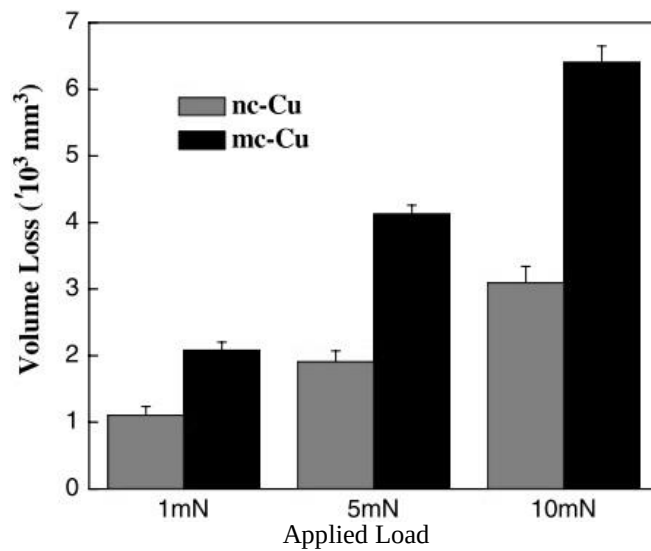


Figure 2.9: Wear volume losses of nc-Cu (56 nm) and mc-Cu (2 μ m) deposits determined during microscratch tests.¹⁷

2.2.1.5 Resistivity

The electrical resistivity of nanograin copper of 10-14 $\mu\Omega$ cm is much higher than bulk copper as shown in Figure 2.10.¹⁹ In thin films this increase is due to electron scattering by phonons, impurities, surfaces and grain boundaries.⁹ Since the number of grain boundaries increases as grain size decreases, there is a higher

resistivity with smaller grained deposits. Kim et al. have had some success in reducing the resistivity of nanograin copper by using reverse pulse plating in which there is an anodic step as part of the pulse plating. They found that reducing the surface roughness helped decrease the resistivity.⁹ Overall low resistivity needs to be balanced with good mechanical properties when using nanograin copper for electrical applications.

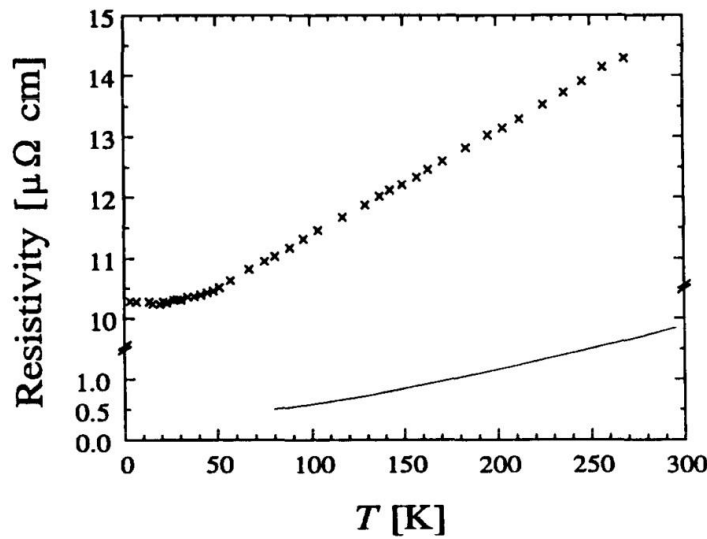


Figure 2.10: The DC resistivity of a nanocrystalline copper sample (top) and the resistivity of a normal copper wire (bottom).¹⁹

2.2.2 Self-Annealing

One issue with using nanograin copper is that grain growth occurs after electrodeposition even at room temperature. This phenomenon is known as self-annealing and is characterized by abnormal grain growth where grains grow by incorporating other grains.²⁰ The grain growth can occur up to months after deposition

and depends on parameters like bath composition, deposition thickness and plating rate.¹⁶ Because it can be difficult to measure grain size directly in a time dependent fashion, many experiments on grain growth measure the resistivity change over time instead.²¹ There are several models such as one by Mayadas and Shatzkes that allow the calculation of the increase in resistivity based on grain size.

The high volume fraction of grain boundaries is the generally-accepted reason for the self-annealing behavior of nanograin copper. There is stored enthalpy associated with grain boundaries which can provide the driving force for grain growth.²² Also, atomic mobility is higher in grain boundaries, so with a high volume fraction of grain boundaries, the activation energy for grain boundary diffusion is lowered. The general equation for grain growth is

$$d^2 - d_0^2 = kt^n \quad (2.1)$$

where d_0 and t are the initial grain size and time, respectively, and k and n are constants. The exponential factor, n , is usually between 0.5 and 1 and is based on the material being deposited.²² While some experimental results show self-annealing follows Equation 2.1, others find that there is an incubation time before growth occurs.²³ Adding organic additives, such as thiourea and other brighteners, to the plating solution gives grain growth that is slow at first, then rapidly increases until it slows down and plateaus.²³ A graph showing this type of growth via the change in resistivity is shown in Figure 2.11.

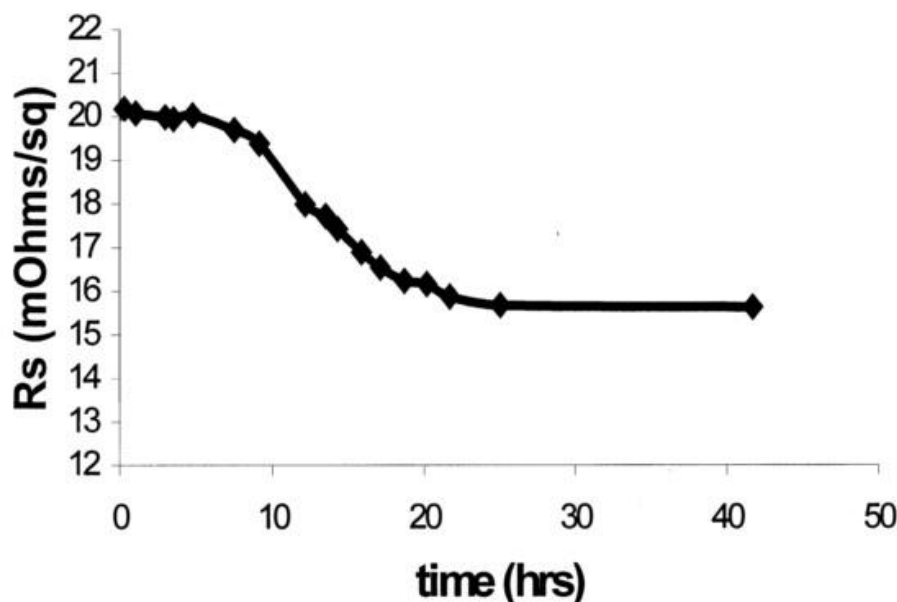


Figure 2.11: Sheet resistance evolution during self-annealing of a 1 μm film.¹⁶

The rationale for this finding is that the additive molecules pin the boundaries in a process modeled by Zener.²¹ Zener's model states that the particles, a general term he uses for molecules, vacancies or other defects that are present in the grain boundaries, lower the energy associated with the grain boundary. These particles can be thought of as providing a counter pressure to the movement of grain boundaries. It is the pinning of grain boundaries that leads to the initial slow growth of the grains called the incubation period.²³ The hypothesis for why the particles stop pinning the grain boundaries is that over time Oswald ripening occurs making the particles larger and more spaced. The larger spacing of the particles leads to less counter pressure and grain growth occurs.²¹ Increasing the amount of additives in the plating solution leads to the deposit remaining at the as-deposited size longer due to the larger number of particles providing a pinning force.²¹ In cases where there is an incubation time

without the use of additives, the reasoning is that there is pinning because of boundary types or other microstructure which is still poorly understood.²¹

By defining the length of time when half of the total grain growth has occurred as the transient time, Harper et al. were able to compare grain growth times for deposits of different thicknesses.²¹ He found that thicker deposits had a shorter transient time than thinner deposits. Also, deposits 1 μm or thicker all showed the same transient time, whereas deposits of thickness around 0.2 μm or under did not exhibit grain growth.²¹ The explanation for this is that there is a density of nucleation sites for grain growth that depends on the thickness of the deposit. As shown in Figure 2.12 Harper et al. have shown a good fit of experimental data for transient time as a function of thickness with the expression:

$$(\tau - t_0) = k/(d - d_0) \quad (2.2)$$

where τ is the transient time, t_0 is the incubation time, k is a proportionality factor, d thickness and d_0 is the minimum thickness where grain growth occurs.²¹

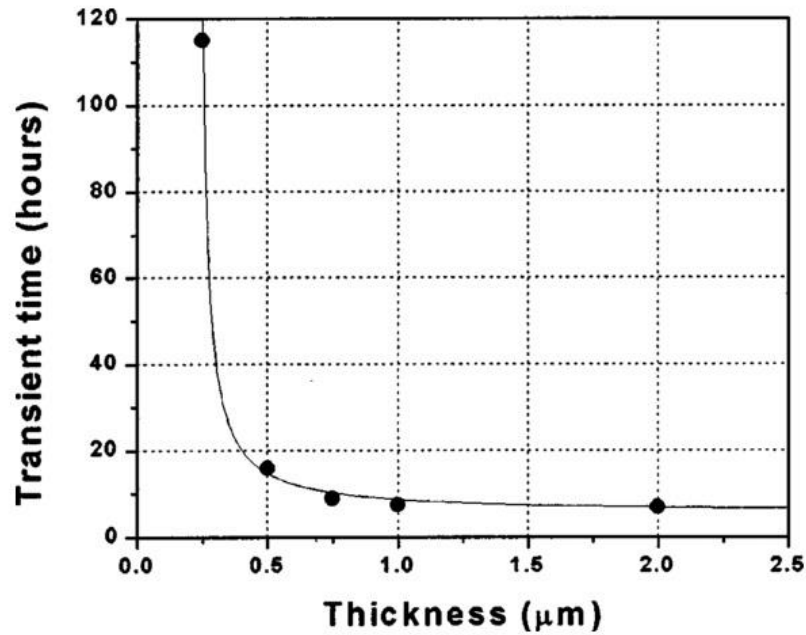


Figure 2.12: Transient time vs film thickness, showing Equation 2.2 with $k = 2.5$, $t_0 = 5.5$ hr and $d_0 = 0.23 \mu\text{m}$.²¹

As plating rate increases, grain growth increases. This is attributed to faster plating giving rise to more defects and smaller as-deposited grains, which have more grain boundaries to drive grain growth.¹⁶

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3. Impinging Jet Electrode System

This section discusses the hydrodynamics and mass transfer characteristics of the impinging jet electrode (IJE) system. Various IJE configurations and current distributions for IJE systems will be reviewed. Also, previous work of our group with the IJE system used in this study will be summarized.

3.1 Impinging Jet Configurations

The main ways of categorizing an impinging jet configuration are: a submerged vs. unsubmerged jet, orientation of the jet to the surface (oblique or normal), the nozzle geometry (circular, slot, or elliptical), one jet or an array of multiple jets, and substrate geometry (convex or flat).¹

In a submerged system the nozzle and substrate are in the plating solution, which can lead to fluid entrainment. Unsubmerged systems, in which the nozzle is not in the plating solution, are less well-studied, but have the advantages of higher rates of mass transfer due to the velocity of the jet remaining large.¹ Another advantage of the unsubmerged system is that current between the cathode and anode is confined to the region where the jet impinges. This leads to more area-selective electroplating. The other aspects of the impinging jet system influence the symmetry of the system, which affects the uniformity of the current distribution.

3.2 Jet Flow Characteristics

The flow of an unsubmerged impinging jet system can be divided into three parts: the free jet region, stagnation flow region and wall jet region as shown in Figure 3.1. The free jet region is near the nozzle and the effects of shear stress and viscosity can be ignored.² The stagnation flow region, also called the impingement zone, is where the vertical kinetic energy is turned into radial energy as the jet hits the substrate. The area of flow with all radial flow is called the wall jet region, which can be subdivided further into three sub-regions: boundary layer flow, fully-developed flow and the hydraulic jump. In the wall jet region, a hydrodynamic boundary layer forms due to viscous drag. Closest to the impingement zone there is boundary layer flow where the thickness of the fluid film is much greater than the boundary layer and can be described by the Blasius solution for flow over a flat plate.³ As the fluid continues to spread radially outward fully-developed flow occurs which is characterized by the boundary layer being the same thickness as the fluid film. At a large distance from the stagnation point there is a sudden decrease in speed and a sudden jump in thickness called the hydraulic jump.⁴

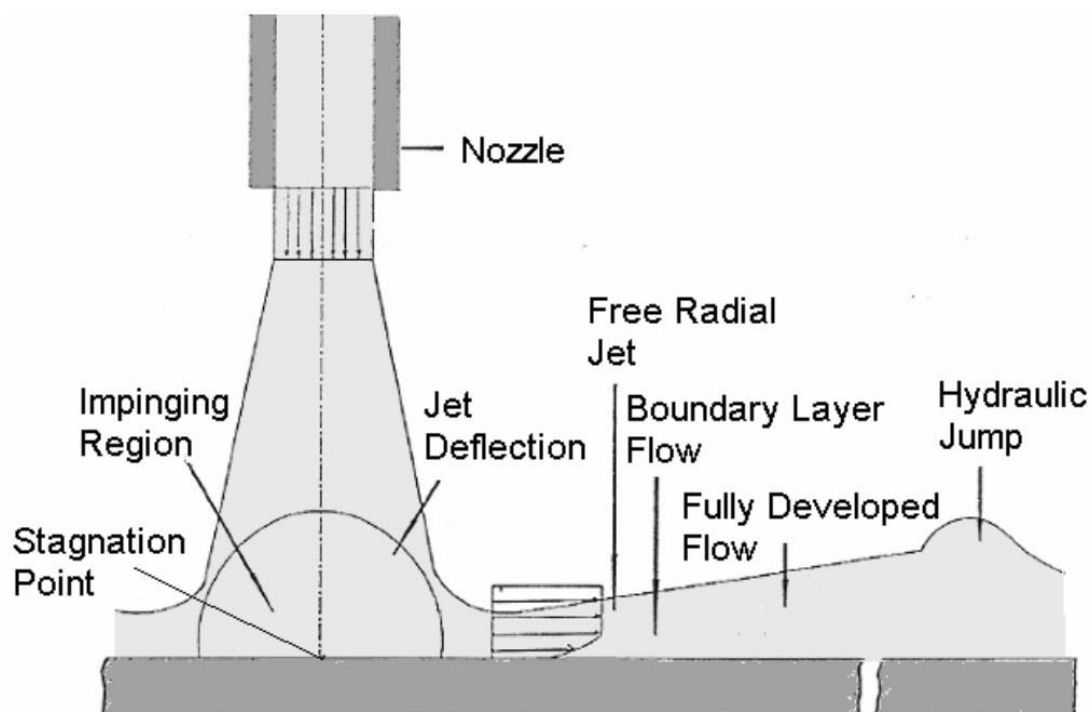


Figure 3.1: Hydrodynamic features and regions of an unsubmerged impinging jet.¹

3.3 Current Distributions

Current density is an important process variable, as it is essentially the rate of reaction. So understanding the current distribution in the experimental conditions is important. A uniform current distribution is desired so that the deposit is as uniform as possible in both grain size and thickness.

Factors that influence the current distribution are cell geometry, electrolyte conductivity, heterogeneous electrochemical kinetics and the reactant transport by diffusion, convection and migration in an electric field.¹ Since the interactions between these variables are difficult to model, it is necessary to simplify the problem

by choosing a set of conditions where the current density is dominated by only one phenomenon. The current distribution is classified as primary, secondary, or tertiary depending on if ohmic, kinetic or mass transfer effects are dominant, respectively.⁵

A primary current distribution is one where the cell geometry is the only determining factor for the current distribution. The amount of current at the electrode for primary current distributions is governed by the voltage, and the ohmic resistance of the solution (R_s).⁵ This means that the resistance to the electrochemical reaction is negligible. When there is non-negligible resistance to the electrochemical reaction, the current distribution is called secondary and is controlled by the kinetics of the electrochemical reaction. A tertiary current distribution occurs when the electrochemical rate of reaction is so high that the mass transport of the species to the electrode controls the deposition. Of these three, the primary current distribution has the most non-uniform current density and is often determined for experiments as it represents the worst case.⁵

Alkire and Chen² modeled the current density for an IJE system based on a simplified flow regime shown in Figure 3.2.

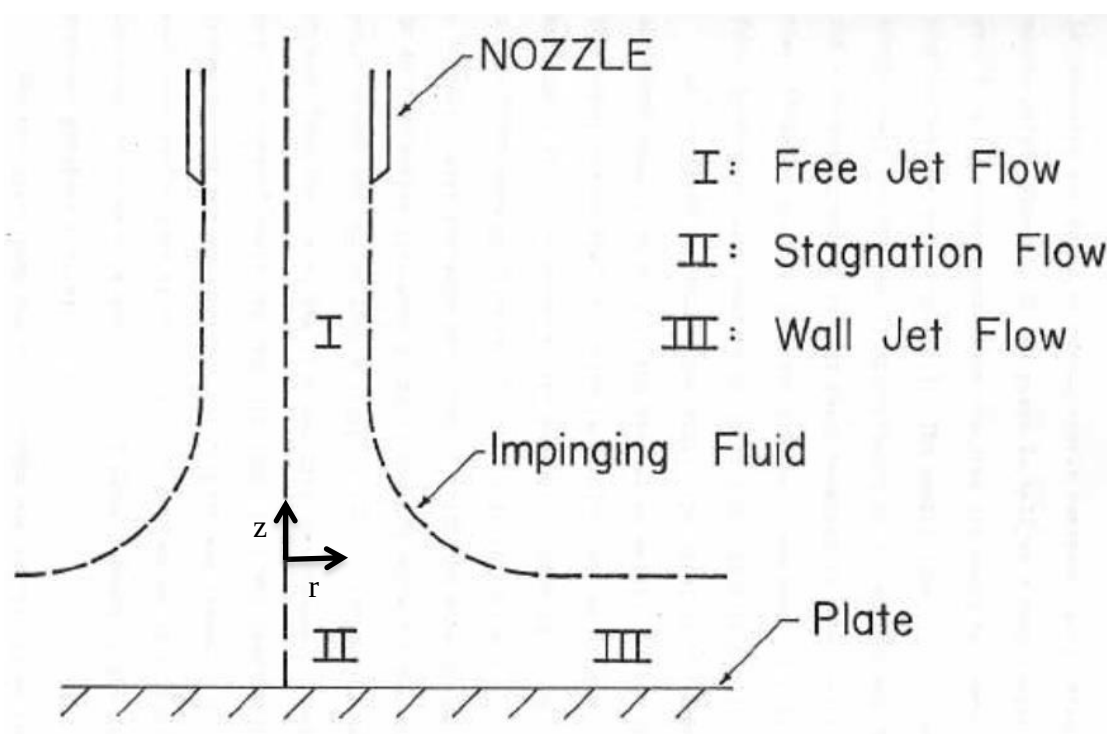


Figure 3.2: Flow regime used for modeling current density for an impinging jet electrode system.²

They assumed that in free jet flow the current density only varied in the z direction. In the wall jet region, since the layer of fluid is thin, the current density is assumed to only vary in the r direction. They arbitrarily chose a division between the two regions to be at $d/2$, where d is the diameter of the nozzle. They also assumed that the mass transport could be described by coefficients obtained from limiting conditions, the system was isothermal, the concentration difference between the inlet and outlet of the cell was negligible and that the physical properties and kinetic parameters remained constant. Ohm's law was used to describe the potential in the wall jet region and Butler-Volmer rate expressions were used to model the

electrochemical reactions. With all their assumptions the final dimensionless expression they found was²

$$J_I + \int_{1/2}^{\infty} 8J_R R dR = \beta \quad (3.1)$$

In Equation 3.1 β is the dimensionless current at the cathode, J_R and J_I are the local current densities in the wall jet region and impingement region, respectively, normalized by the limiting current density in the impingement zone, and R is the dimensionless radial position from the stagnation point.² To solve equation 3.1 an iterative numerical method based on finite differences was used.

Using experiments with segmented electrodes Alkire and Chen found that in agreement with their model, there was a region of “uniform accessibility” from the center of the impingement zone to about $d/2$ where thickness and current distributions are uniform along with the concentration of the metal ions.¹ An example showing a region of constant current density near the impingement zone is shown in Figure 3.3. This finding of a region of “uniform accessibility” means that by masking off the area outside the impingement zone the plating should proceed at a near constant rate over the substrate that is exposed. The masking might mean an increase in plating rate near the mask edge, but this effect is typically small compared to the drop in current density in the wall jet region.¹

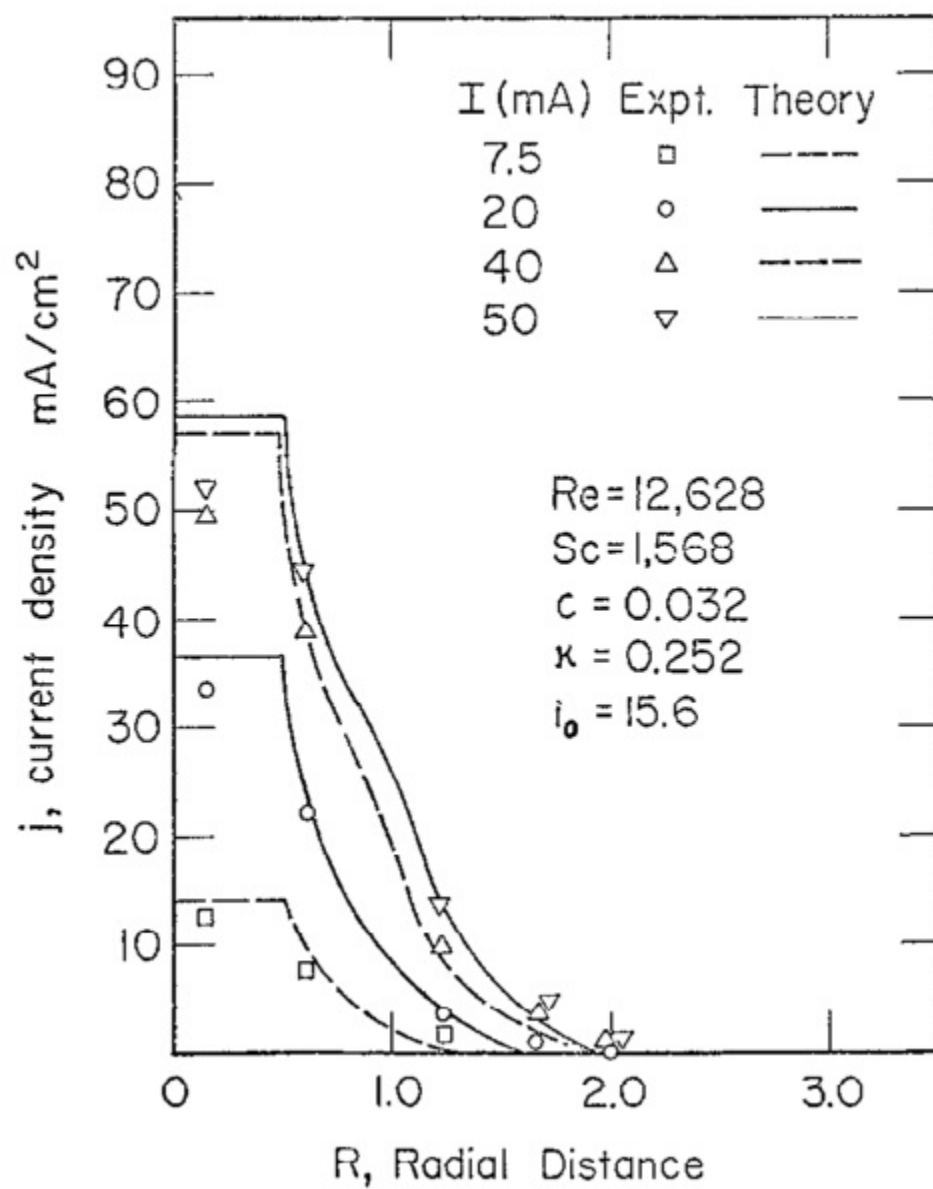


Figure 3.3: Effect of applied current on distribution near the impingement region for ferricyanide reduction.²

3.4 Mass Transfer

Impinging jet systems show high rates of mass transfer and regions of uniform accessibility.⁶ The mass transfer from an unsubmerged impinging jet to a flat surface was studied by Chin and Hsueh.⁶ They used a Chilton-Colburn analogy of comparing momentum transfer to mass transfer to obtain the following:

$$\overline{Sh} = 0.9Re^{1/2}Sc^{1/3}(H/d)^{-0.09} \quad (3.2)$$

as a model for the mass transfer when $r/d < 0.8$, and $0.5 < H/d < 5.0$. Sh is the Sherwood number (kd/D where k is the convective mass transport coefficient, D the diffusivity and d the nozzle diameter), Re is the local Reynolds number (Vd/ν where V is the exit velocity of the nozzle, and ν is kinematic viscosity of the solution), Sc is the Schmidt number (ν/D) and H is the nozzle height above the substrate.²⁵

3.5 Review of Previous Work

This section summarizes the previous work of our group by Osborne^{7,8}, Thiemi⁹, and Sweet¹ with the IJE system used in this study. This work was focused on electrocodeposition, where particles were incorporated into the deposit during deposition, using the IJE.

Osborne designed and built the current IJE system to study Al_2O_3 electrocodeposition with copper under the limits of operation for the system. He also studied some properties of the deposits made under various plating conditions. The main variables Osborne investigated were flow rate, particle loading, current density and particle size.

Osborne found that particle incorporation was highest for flow rates between 2.5 and 3 L/min with higher particle incorporation for smaller particles. Current density was found to have the greatest effect on particle incorporation with higher incorporation seen with lower current density for 50 nm particles, but higher current density needed for 1 μm particles. For particle loading a linear relationship of increasing particle loading corresponding to higher particle incorporation was found. With a current density of 200 mA/cm^2 and a flow rate of 2.5 L/min, a deposit with an average grain size of 175 nm with many grains less than 100 nm was made. SEM images from Osborne's work are shown in Figures 3.4 and 3.5, which show that different plating conditions give different microstructures. Figure 3.4 shows an even distribution of particles over a background deposit with smooth edges. In contrast Figure 3.5 shows a jagged microstructure without visible particles.

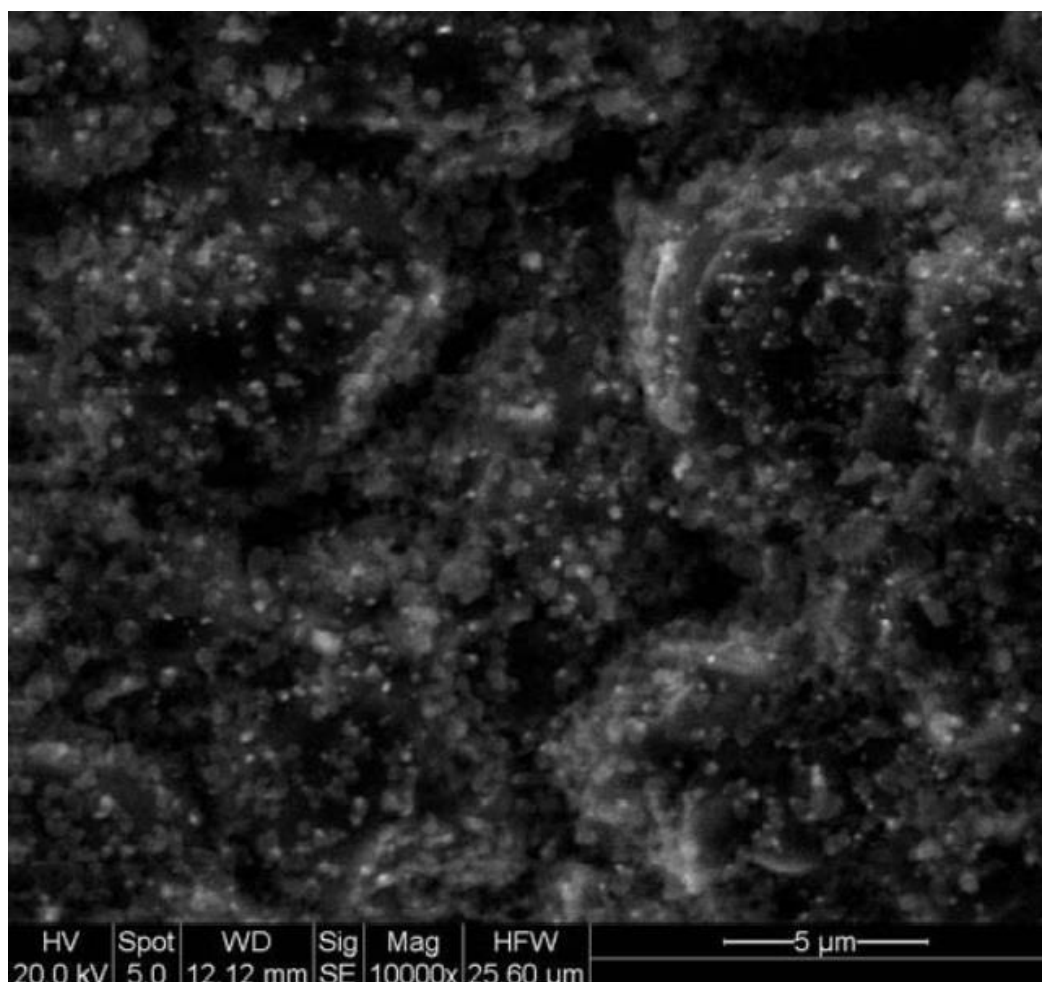


Figure 3.4: SEM image of a composite film made at 150 mA/cm^2 and 2.5 L/min with a $1.0 \text{ M CuSO}_4 + 1.2 \text{ M H}_2\text{SO}_4$ electrolyte bath.⁷

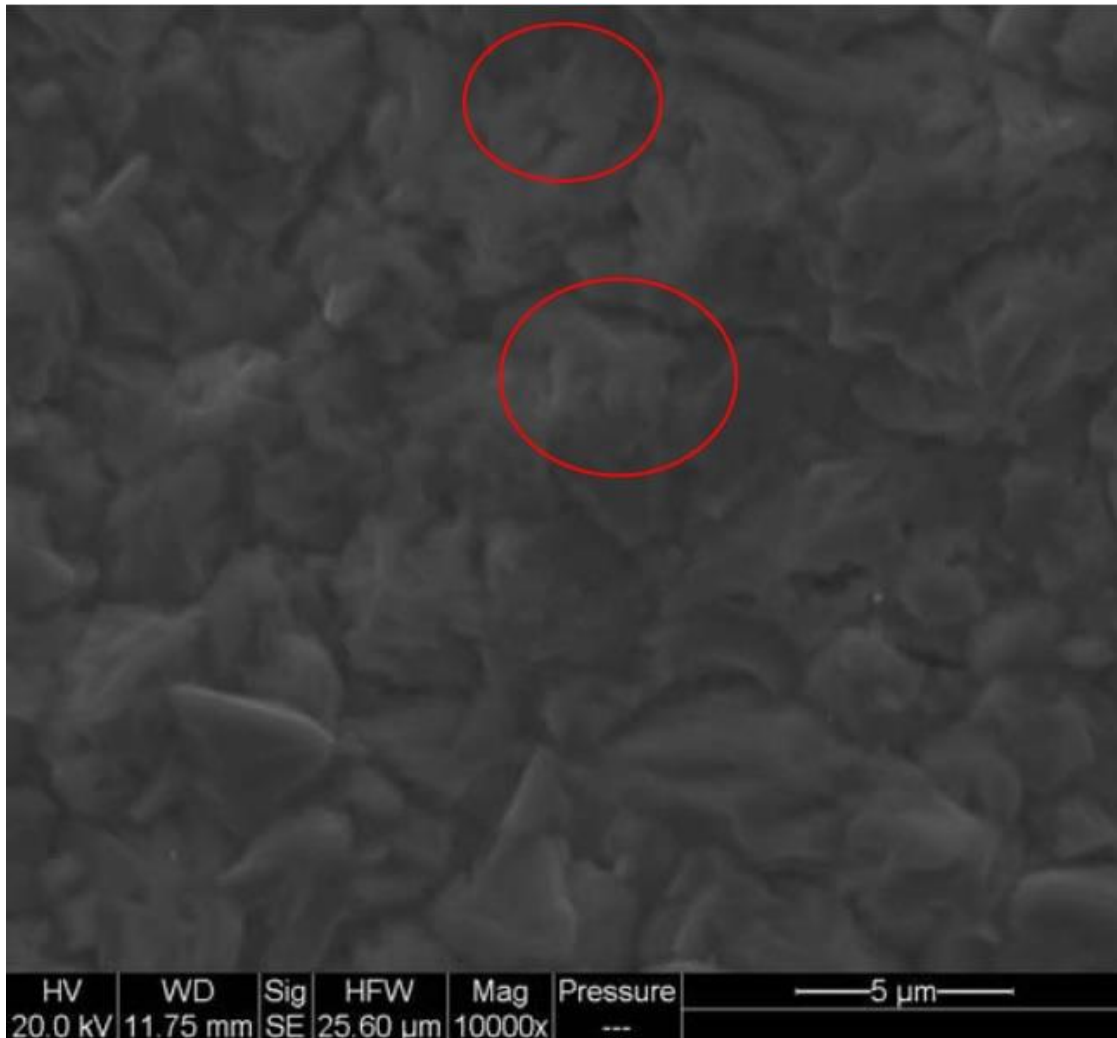


Figure 3.5: SEM image of a composite film made at 50 mA/cm^2 and 7.0 L/min exhibiting a jagged microstructure with dendritic features in circles.⁷

Osborne also found that with increased current density there was an increase in electrical resistivity and hardness of the deposited films, which may be attributed to grain size refinement.

Thiemig et al.⁹ did more characterization of the $\text{Cu/Al}_2\text{O}_3$ deposits made with the IJE system by measuring the microstructure, hardness, grain size and distribution of particles. He found that the Al_2O_3 particles were randomly distributed and that the

morphology of the deposits could be either smooth or nodular depending on plating conditions. SEM images showing these different morphologies are shown in Figure 3.6.

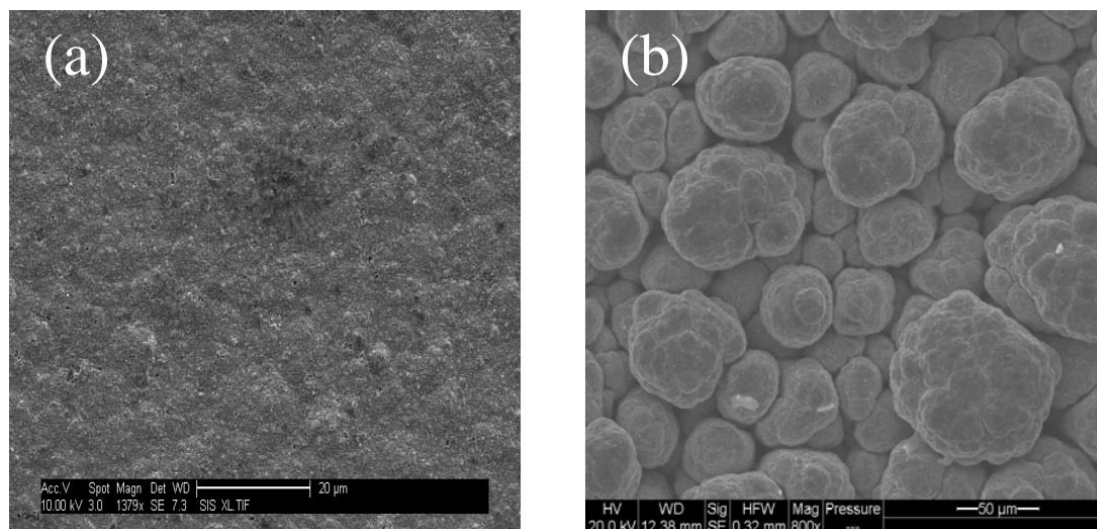


Figure 3.6: SEM images of films of Cu-50 nm alumina (a) from 1.0 CuSO₄ bath with 160 g/L loading at 125 mA/cm² and (b) from 0.1 M CuSO₄ bath with 120 g/L loading at 67 mA/cm².⁹

Thiemig et al. also found that as the current density increased for pure copper deposits the grains which were oriented in mainly one direction (100) tended to become less ordered with other grain orientations appearing. He also found that it was possible to have an average grain size less than 100 nm when plating pure copper as shown in Table 3.1.

Table 3.1: Crystallite size and microhardness of pure copper and copper-alumina nanocomposits.⁹

Current Density (mA/cm ²)	Particle content (wt %)	Crystallite size (nm)	Microhardness (HV)
10	0	79	100.4
75	0	68	138.2
10	8.2	58	182.9
175	3.2	37	241.7

Sweet¹ conducted experiments with the IJE system to determine the limiting current density of the system. Sweet also expanded on Osborne's work investigating particle loading, current density, flow rate, the concentration of copper sulfate, pH, and particle phase and size. In agreement with Osborne's findings Sweet found a linear relationship for particle incorporation versus particle loading over a wider range of values. It was also found that α -alumina particles had lower incorporation rates than γ -alumina particles. Sweet also presented her incorporation results with current density normalized with limiting current density as shown in Figure 3.7, which shows that for all copper sulfate concentrations there is higher particle incorporation at lower normalized current density.

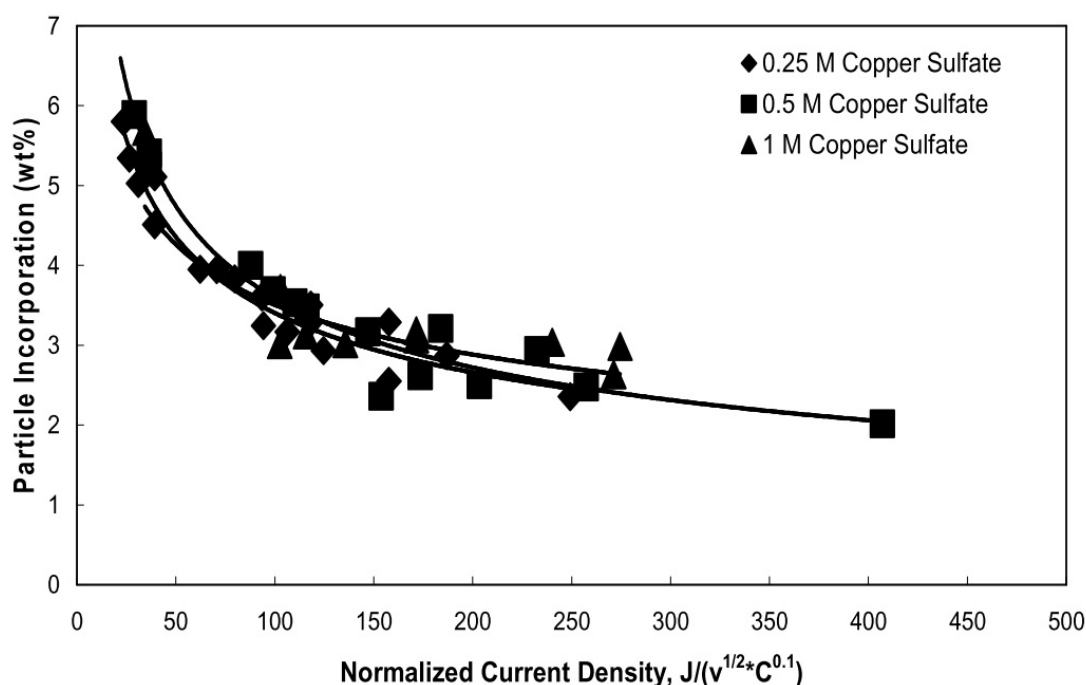


Figure 3.7: Particle incorporation vs normalized current density for various copper sulfate concentrations.¹

3.6 References

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4. Experimental Procedure

The main variables studied during electrodeposition were current density, flow rate and type of substrate. The current density was 10 mA/cm² or 200 mA/cm², while the flow rate was 2.5 L/min or 7 L/min, which are essentially the limits of operation. Both platinum and nickel substrates were used. A 1 M copper sulfate bath at a pH of 1.5 was used for all experiments to compare with previous work by Thiemig et al.¹

4.1 Experimental Apparatus

The impinging jet electroplating experimental apparatus was designed and built by Dr. Steve Osborne.² An overview of the final design specifications and requirements is included here and details can be found in Osborne's PhD dissertation.² The major design requirements were that the apparatus needed to be able to control the hydrodynamics and current densities of the deposition, while being corrosion and wear resistant to low pH solutions (pH <2) that could contain abrasive alumina particles. Another requirement taken into account was that the apparatus needed to recycle solution to reduce waste created during experimentation.²

Figure 4.1 shows a schematic of the experimental setup used in these experiments. The apparatus consists of a reservoir tank, with an outlet ball valve near the bottom. This valve allows for the electric diaphragm pump to be flushed with clean water after runs while the plating solution remained in the reservoir. The outlet of the pump has a tee connector leading to two ball valves that control the flow through the process loop and the bypass loop. The process loop has a paddle wheel flow meter

before the fluid flows into the jet nozzle, while the bypass loop allows fluid to flow directly into the tank. From the jet nozzle the fluid impinges onto the substrate and then flows into the reservoir. A galvanostat is used to control the current density and wires are attached to the jet nozzle, which acts as the anode, and the substrate via a wire in the substrate holder. Figure 4.2 shows a photograph of experimental set up.

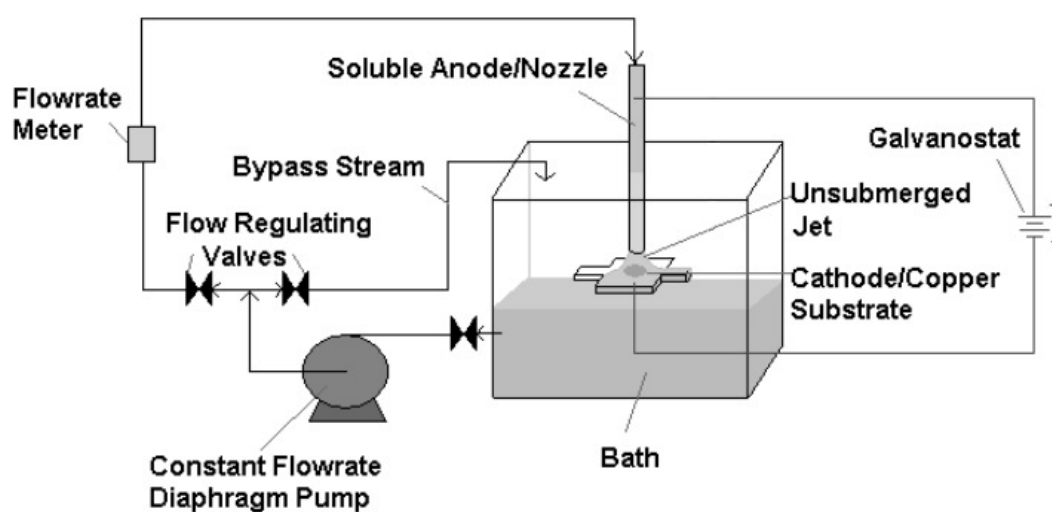


Figure 4.1: Schematic of the impinging jet electroplating system.³

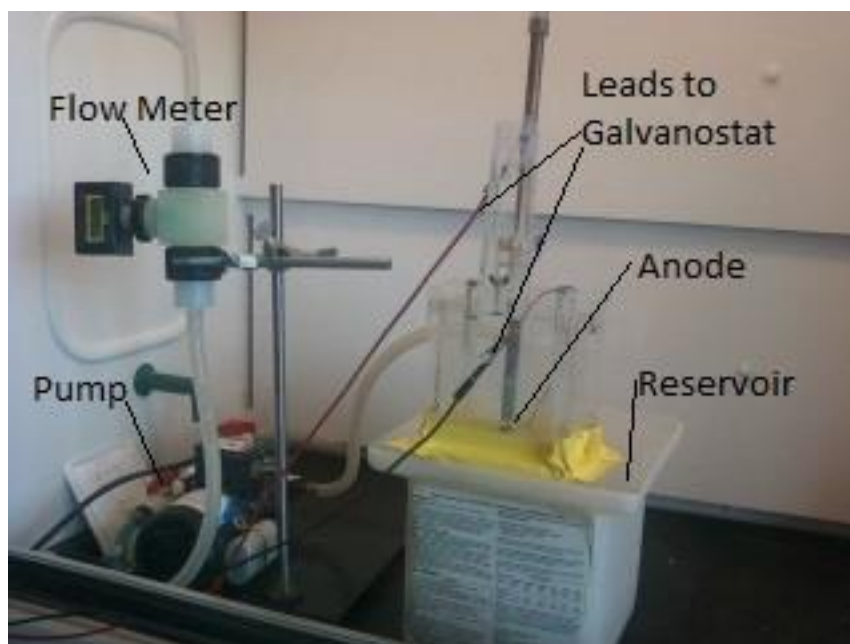


Figure 4.2: Photo of the experimental setup

4.1.3 Electrochemical Cell Geometry

For these experiments, the impinging jet was unsubmerged, circular, normal to the substrate, unconfined and flowing in the direction of gravity. This section will describe the electrochemical cell. Figure 4.3 shows the setup of the substrate, nozzle and substrate holder. The nozzle was held above the substrate holder with plastic rods inside a plexiglass box. The substrate holder was screwed into the rods to hold it in

place during deposition and the substrate was attached with electroplaters' tape.

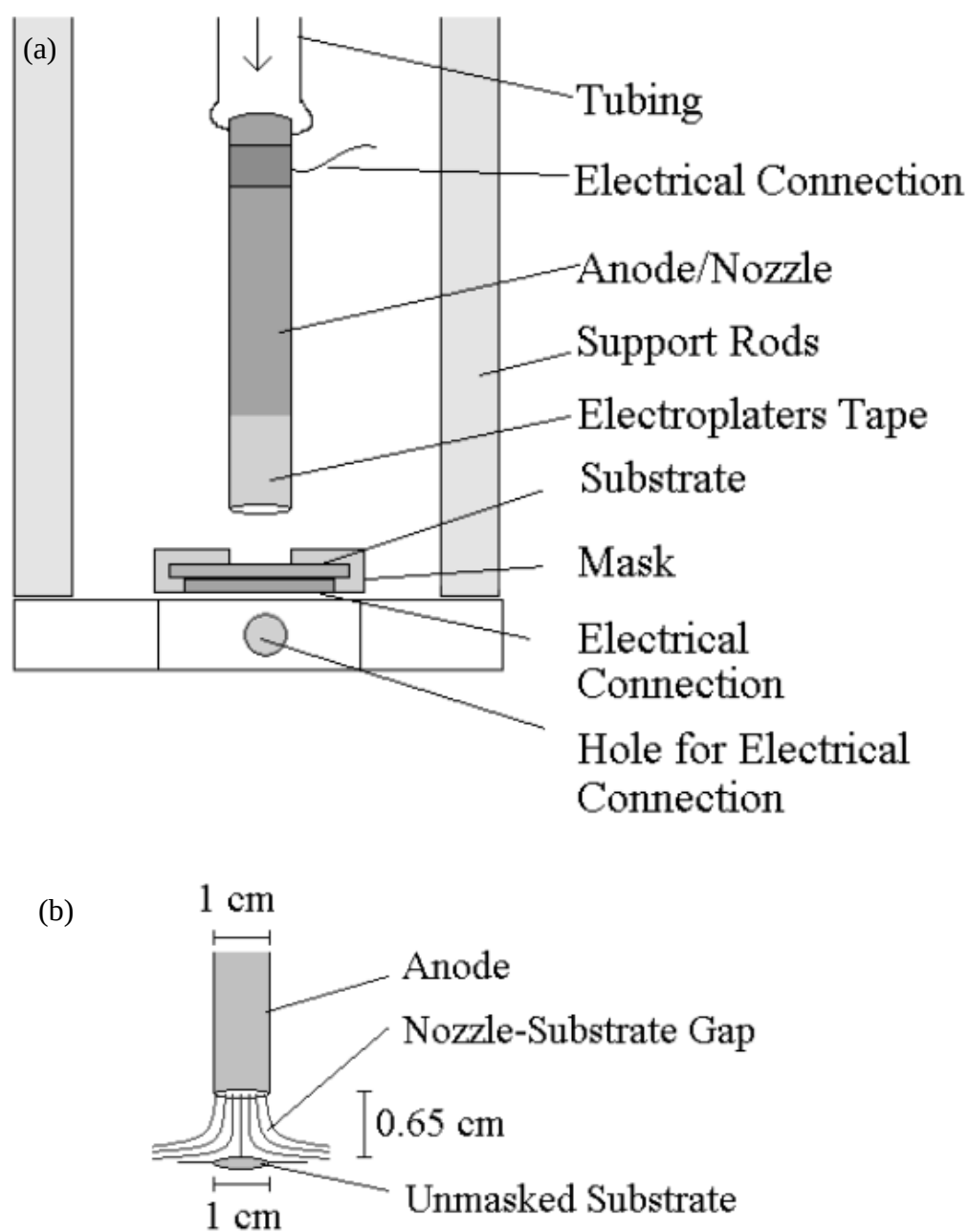


Figure 4.3: Schematics of the plating apparatus in the impinging jet region, showing (a) the substrate holder in relation to the anode and (b) the flow of the fluid from the anode to the unmasked substrate.³

The anode was a soluble copper nozzle, such that the anodic reaction was the electrochemical dissolution of copper to Cu^{2+} . The electrical and hydrodynamic requirements included that there needed to be a continuous stream of liquid to the cathode to minimize ohmic resistance from a poor connection between the cathode and anode. To keep current density constant and to reduce the vena contracta effect required that the cross-sectional area of both the nozzle and exiting stream change as little as possible. Taking into account these requirements, Osborne decided a strait copper pipe was the ideal anode.²

The copper pipe was Alloy C-12-200 from Mueller Industries, Inc. with an outside diameter of 1.27 cm and an inside diameter of 1 cm. It was determined that this alloy with a composition of 99.9 wt% Cu and 0.02 wt% P was needed since alloys with less phosphorous lead to dendrites forming in the tube.² Osborne found that a pipe length of 8-12 in. was needed to have the tube fit securely in its plexiglass holder and it also minimized flow disturbances from the acrylic tubing to pipe transition.

To make an electrical connection with the galvanostat, a piece of copper wire was securely taped to the pipe with a portion available for an alligator clip to grasp. Since the length of the tube changes slightly during deposition electroplaters tape was wound around the end of the pipe before the position of the pipe was adjusted so the nozzle substrate gap was 0.65 cm. This tape both kept the nozzle substrate gap constant and made it clear when the copper pipe had changed length enough that its position needed to be readjusted. The tape was trimmed to the new pipe length whenever the height of the pipe decreased due to anodic dissolution.

For the cathode, the requirements of the substrate holder were that there could be no buildup of fluid during deposition, deposition could only happen on the substrate and that the substrate had a secure and easy electrical connection.² Figure 4.4 shows the substrate holder which was made of 0.5 inch thick acrylic sheet and had a square center for the substrate with holes in it for a wire to pass through and extending tabs with holes in them to allow the holder to be screwed into the acrylic dowels that are part of the anode set up.

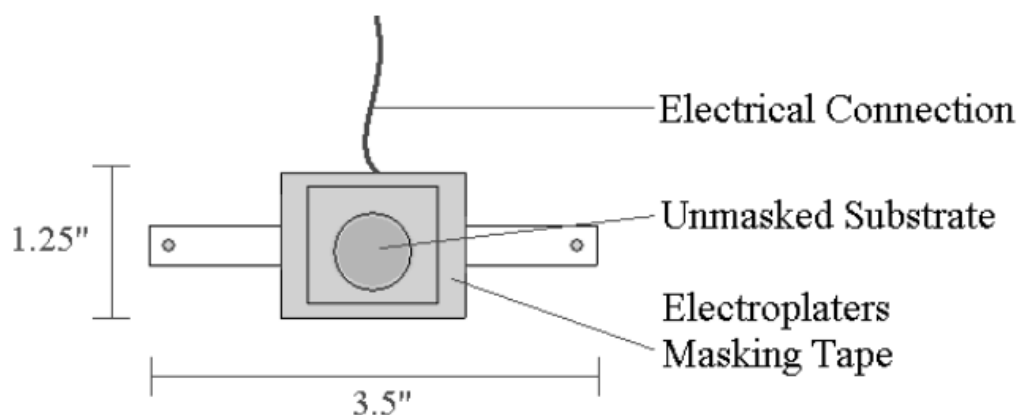


Figure 4.4: Schematic of the substrate holder.²

The substrate holder had to keep the substrate at the correct distance (0.65 cm) and angle (90°) which were chosen to be consistent with previous experiments by Sweet³, Osborne² and Thiemig¹. For the electrical connection, a piece of copper wire was soldered to a sheet of copper that the substrate was taped to during deposition. The sheet of copper was embedded in the center of the holder so it was flush with the acrylic and the wire was threaded through the hole. The wire had to be encased in a low density polyethylene (LDPE) tube that was slightly larger than the wire to protect the wire from the acidic bath. Without this protection with the LDPE, the wire

insulation cracked and undesired depositions occurred on the wire. The wire and underside of the copper sheet were sealed using epoxy.

When an experiment was run the substrate was taped onto the copper sheet with 3M electroplaters' tape. The tape was cut to a size large enough to cover the entire top and sides of the 1.25 in X 1.25 in square central area of the holder and smoothed down to insure good adhesion. Using an X-acto knife and an acrylic template, a 1 cm diameter hole was cut in the tape above the center of the substrate. This hole was placed in the impingement zone so that deposition was limited to this circular area. For the platinum substrate the hole in the tape had to be cut before the tape was put on the holder, because the platinum was so thin the X-acto knife would cut through it as well.

4.1.1 Hydrodynamic Control

The fluid was circulated through the process loop at a controlled rate between 2.5 and 7 L/min, which were the limits of the pump. An electric diaphragm Jabsco model 31801-0115 continuous duty pump was used. This pump was used because it has minimal wear surfaces that come in contact with the bath to reduce wear and contamination of the bath.² Another advantage of this pump is that it is self-priming so it was easy to start the fluid flow. The power of the pump made it necessary to include a bypass loop to achieve lower flow rates through the nozzle. The process loop and bypass loop flow rates were controlled by ½" PVC ball valves. The flow rate in the process loop was measured with a Blue-White Industries F-1000-RB digital paddle

wheel flow meter, with a range of 1-10 L/min and accuracy of 0.01 L/min. Acrylic tubing, Cole-Parmer model 06422-16, was used to connect the reservoir, pump, flow meter and nozzle.

The reservoir was a Saint-Gobain 8 L high density polyethylene (HDPE) rectangular tank. A plexiglass cover fit on the top of the tank to prevent splashing and minimize evaporation of the solution. The cover had a built-up box that the nozzle fitted in and a hole for a stirrer to pass through. However, a stirrer was not necessary for these experiments, so the hole for the stirrer was covered with parafilm. One important feature of this set up is that there was a single reservoir so that the plating solution was recycled and the impingement of the nozzle onto the substrate was done above the reservoir so there was no hydrodynamic contribution from the eddies in the reservoir fluid.

4.1.2 Current Density

An EG&G Princeton Applied Research potentiostat/galvanostat Model 273 was used to control the current during deposition. It was run in galvanic mode to compare with results from previous experiments.^{1,3}

The galvanostat had an internal coulometer that measured the charge that passed through the system. The same amount of charge, 64 C, was passed through the circuit for each deposit so that the same amount of material would be deposited, which was 21 mg and corresponded to a deposition thickness of 30 μm based on 100%

efficiency. The amount of charge need to obtain a 30 μm deposit to compare with Thiemig et al. was found using Faraday's Law

$$m = \frac{QM}{Fz} \quad (4.1)$$

where m is the mass deposited assuming 100% efficiency, Q is the charge passed through the system, M is the molar mass of the copper (63.5 g/mol), F is Faraday's constant (96485 C/mol) and z is the number of electrons transferred (2). The thickness of the sample from a given mass was found using

$$t = \frac{m\rho}{\pi d^2/4} \quad (4.2)$$

where t is the thickness of the deposit, m is the mass, ρ the density (8.96 g/cm³) and d is the diameter of the unmasked circle (1 cm).

Leads from the galvanostat were clipped to wires attached to the substrate and anode to make an electrical connection. The galvanostat has different current ranges that can be used, so the current range was always checked prior to running an experiment. The 10 mA range was used for the 10 mA experiments and the 100 mA range was used for the 200 mA experiments. The applied current was controlled within ± 1 mA, the coulometer was accurate to ± 0.01 C and the potential to ± 1 mV. Potentials measured in the experiments ranged from 0.5 V to 2 V in reference to the soluble copper anode. A reference electrode was not used because it would interfere with the hydrodynamics³.

4.2 Deposition Procedure

This section includes procedures for cleaning the apparatus, making the electroplating bath, preparing the substrate and the actual deposition. These procedures were necessary for reproducible experiments.

4.2.1 Apparatus Cleaning Procedure

To clean the apparatus before a new set of tests was run the following procedure was used. The tank was emptied of liquid and then the tubing was carefully removed so as to minimize any leakage of the solution that was still in the tubes. The tank and each tube were scrubbed to remove any precipitate that had formed and then rinsed out with water. To clean the pump, clean tubes were attached to the inlets and outlets and clean water was run through the pump flushing out any remaining solution. This was done until the water exiting the pump was clear. After all components had been cleaned and dried they were reassembled to run the next experiment.

4.2.2 Electroplating Bath

A solution of 1 M copper sulfate with a pH of 1.5 was used for all experiments. The copper sulfate was $\text{CuSO}_4 \cdot \text{H}_2\text{O}_5$ from Fisher Scientific and the pH was adjusted with H_2SO_4 from EMD. Generally 4 L of solution was made at a time since it was the least amount of solution that would fill the reservoir without introducing air into the tubing and for waste minimization. The calculated weight of copper sulfate needed was weighed with a Sartorius model 1712 MP8 Silver Edition balance to within an

accuracy of ± 0.01 g. This copper sulfate was added into a large plastic container with a magnetic stirrer bar in the center and a little less than the total amount of DI water needed was added. This was stirred with the magnetic stirrer until the salt dissolved.

To attain the desired pH of 1.5, sulfuric acid was added slowly to the solution while the magnetic stirrer was still slowly stirring. The pH was checked after each addition with an Orion Model SA 720 pH meter until the desired value was reached. Once the bath composition was attained, the solution was carefully poured into the reservoir and was ready for use.

4.2.3 Solution Storage

To minimize waste, the solution was re-used or stored. If experiments were run on consecutive days the bath was allowed to stay in the reservoir, but the holes and edges of the top were covered in plastic to reduce evaporation. For longer breaks, the solution was drained into a glass bottle that was sealed to prevent evaporation. Each day the pH of the solution was checked and adjusted as needed before experiments were run. The copper concentration was not adjusted as it remained constant due to the electrochemical dissolution of the copper anode during experiments, which matched the electroplated amount of copper.

4.2.4 Substrate Preparation

Two different substrates were used for these experiments, nickel and platinum. The nickel was $\geq 99.9\%$ pure from Aldrich and 0.125 mm thick. The platinum was

donated to the lab by Dr. Arrhenius at UCSD and was 0.01 mm thick. X-ray diffraction (XRD) was used to check composition and purity of the platinum which was found to be $\geq 99\%$ pure. Osborne¹ and Sweet² used copper substrates but since X-ray diffraction was going to be used to examine the deposits a copper substrate could not be used because the XRD would not be able to tell the difference between the deposit and the substrate. Platinum was chosen as a substrate based on its use in literature.⁴ When deposits on platinum did not give expected results nickel was chosen as a substrate based on its similarity to copper.

For each experiment the substrate was cut to approximately 1.2 cm X 1.2 cm square. The substrate was soaked in isopropanol for 20 minutes and then let to air dry. The substrate was then put on the substrate holder as described in Section 4.1.3.2.

4.2.5 Deposition Procedure

To run a deposition, first the electroplating bath and the substrate were prepared as described previously. The substrate and substrate holder together were weighed twice to get an initial weight. Weighing was done to check that the same amount of material was deposited for each deposition. The substrate holder was then screwed into the acrylic dowels and put into place on the apparatus. The cables from the galvanostat were attached to the wires on the anode and cathode. Then the valve on the tank was checked to make sure it was in the open position and then the pump was turned on. Using the two valves, the flow rate was adjusted to the desired rate. The desired current was programmed into the galvanostat and the charge counter was

cleared before turning the current on. While the deposition was running it was necessary to watch the flow rate and galvanostat indicators to insure everything was working properly. When 64 C of charge had passed through the system the current was turned off, followed by the pump. The substrate holder was unscrewed and the substrate was rinsed with DI water. The substrate holder was allowed to thoroughly dry in air; then it was weighed again twice before the tape was carefully removed and the substrate released. The substrate was labeled and was then analyzed.

4.2.6 Trouble Shooting

The most common problem that occurred while running an experiment was the voltage (E) overload light on the galvanostat would indicate. This signals that there is too much resistance in the circuit. Once the E overload light lit, the experiment was no longer valid because the galvanostat was no longer able to fully control the circuit so that the voltage and current readings may have been incorrect.⁵ To determine the cause of the additional resistance in the circuit, an ohm meter was used to measure the resistance between different parts of the circuit while it was running. The most common causes for the high resistance were the cables connecting the galvanostat to the circuit and the copper pipe that is the anode. If the cables were the problem they were switched with other cables. The copper pipe built up rust, which was cleaned off with acid and sanding. The wire in the substrate holder could also break, which would disconnect the electrical circuit. This was solved by either switching to a different substrate holder or by removing the epoxy that holds the wire in place and putting in a

new wire and allowing the new epoxy (5-minute, Devcon #14250) to harden for 24 hours.

Another problem that was encountered was the pump failing to keep the solution flowing at the same flow rate for the whole experiment. This was countered by adjusting the flow valves throughout the experiment to keep the flow rate as close as possible to the desired value.

While the weighing the samples before and after was used as a confirmation that the same amount of material was being deposited, this would sometimes give results that more copper was deposited than expected. This was found to be a problem with the drying process. It was easy for the DI water used to rinse the holder and solution to seep into crevices formed when molding the tape around the holder and this would not evaporate as fast as the surface water leading to excess weight. The solution was to allow the substrate to dry longer to ensure an accurate weight.

4.3 Analytical Methods

Various methods were used to analyze the deposits. These included scanning electron microscopy (SEM) to examine at the samples with a high degree of magnification, x-ray diffraction to measure the composition of samples and the platinum substrate and computer analysis to measure the grain size from SEM images.

4.3.1 Scanning Electron Microscopy Analysis

Scanning electron microscopy (SEM) was used for the analysis of grain structure and size. Two different SEM's in the UCSD NANO3 facility were used; the FEI XL30 Ultra High Resolution Scanning Electron Microscope (UHR SEM) was used for the deposits on platinum since it has better resolution, and a FEI Quanta 600 Environmental Scanning Electron Microscope (ESEM) was used for the deposits on nickel because magnetic materials cannot be analyzed by the UHR SEM. The procedure for using the SEM was the same for both the platinum and nickel samples. The sample was placed on a standard SEM base and attached with conductive carbon tape. After scanning the whole deposit approximately 5 images were taken at various magnifications in representative areas of each sample.

4.3.2 X-Ray Diffraction Analysis

To check the purity of copper deposits and the platinum substrate a modified General Electric X-ray Diffractometer with monochromatized $\text{CuK}\alpha$ radiation was used. The following procedure was used. The sample was secured into a holding plate with petroleum jelly, then the holder was placed in the XRD machine. A scan of $0.12^\circ/\text{min}$ was performed over the 2-theta range from 10° - 100° . The XRD signal graphs were compared with the peaks from standard graphs.

4.3.2 Determining Grain Size

In order to determine grain size a combination of hand and computer analysis was done on the SEM image with the highest magnification for each sample. The program ImageJ⁶, a free image-processing program, was used to automatically determine the area of each grain. The SEM images did not have enough contrast for ImageJ to find the edges of the grains by itself even with extensive computer manipulation. The solution was to outline each particle by hand with dark ink on a picture that was printed to scale. An example of a hand outlined image is shown in Figure 4.4. The outlined pictures were then scanned and the software was able to be used for the grain size analysis. Only grains that were fully inside the area of view were used to avoid underestimating the grain size. Effective grain diameters were calculated assuming all the grains were perfectly circular so that grains with very different shapes could be compared with a standard measurement. The equation used to calculate grain diameters was

$$d = \sqrt{\frac{4A}{\pi}} \quad (4.1)$$

where d is diameter and A is the area of the grain. To confirm the computer analysis, the diameters of a few mostly circular grains were measured both by hand and by the computer. These measurements for the diameters were found to agree to within 1 nm. The average grain size was calculated by adding up the grain sizes of all the particles and dividing by the number of particles in the SEM image.

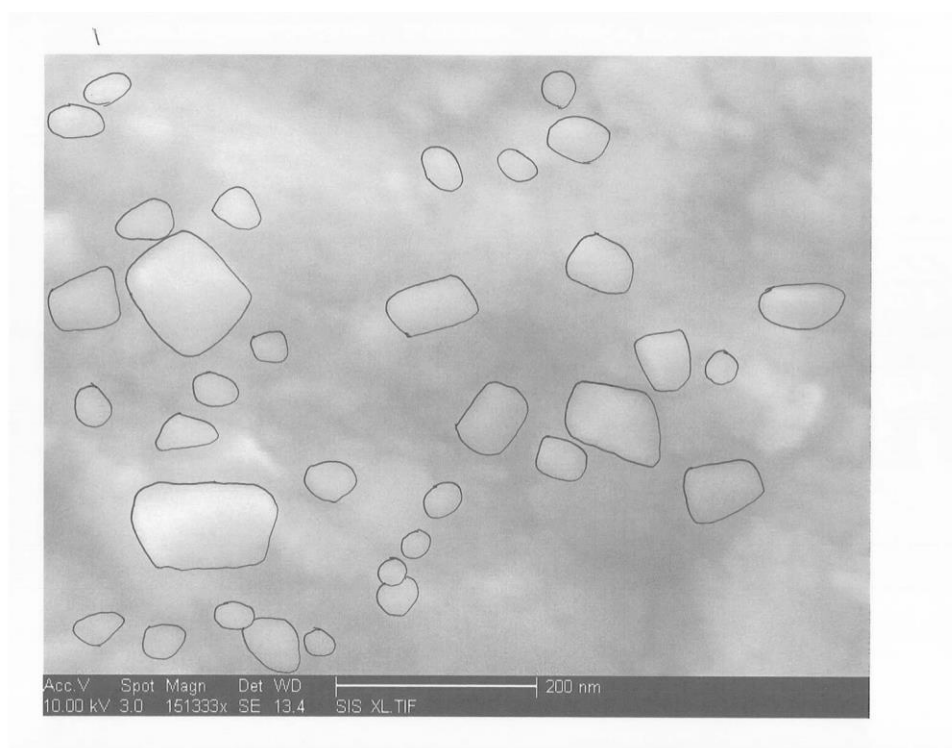


Figure 4.5: Hand outlined SEM image of sample N1 taken 15 days post-deposition.

4.4 References

1. Osborne, S. J. Electrocodeposition of Nanoparticle Composite Films Using an Impinging Jet Electrode, University of California, San Diego, 2006.
2. Sweet, W. S. Investigation of Electrocodeposition Using an Impinging Jet Electrode, University of California, San Diego, 2006.
3. Thiemig, D., Osborne, S. J., Sweet, W. S., Talbot, J. B. Electroplating of Copper-Alumina Nanocomposite Films with an Impinging Jet Electrode. *ECS Transactions* **2008**, 11, 35–44.
4. Ghosh, S. K.; Grover, A. K.; Dey, G. K.; Totlani, M. K. Nanocrystalline Ni-Cu Alloy Plating by Pulse Electrolysis. 2000, 48–63.

5. EG&G Princeton Applied Research Model 273 Potentiostat/Galvanostat Operating Manual **1985**.
6. ImageJ, Image Processing and Analysis in Java. <http://rsbweb.nih.gov/ij/>, 10/18/2012.

5. Results and Discussion

This section discusses the morphology and grain sizes for 3 copper deposits made on platinum and 4 deposits made on nickel using the IJE system at the limits of operation of the IJE system. The purpose was to investigate if grain sizes of less than 100 nm could be achieved and the effect of flow rate and current density on grain size and morphology. Since self-annealing has been reported to occur in nanograin deposits of copper,¹⁻⁴ representative SEM images were taken at 15, 38 and 230 days post-deposition to investigate if self-annealing occurred.

The process conditions that were used were flow rate of 2.5 or 7 L/min and current density of 10 or 200 mA/cm², which were at the low and high limits of operation of the IJE system. All deposits were made with a plating solution of 1 M CuSO₄ at a pH of 1.5 and were deposited to a thickness of about 30 µm based on the process parameters used in previous work by Thieming⁵ that showed grain sizes of less than 100 nm. Since the deposit thickness was not measured during deposition the deposition was stopped when 64 C of charge had passed through the system. A final charge of 64 C is equal to a deposited thickness of 30 µm assuming 100 % current efficiency, which was found previously⁶.

The surfaces of the rinsed platinum and nickel substrates were similar as shown in the SEM images in Figure 5.1. The platinum substrate was a fairly smooth surface with a few imperfections, while there is some evidence of ridges in the nickel substrate. On the macro-scale the nickel substrate looked smooth while the platinum substrate had ridges on it. However, the morphology of the copper films deposited on these substrates under the same plating conditions with the IJE were quite different as will be discussed.

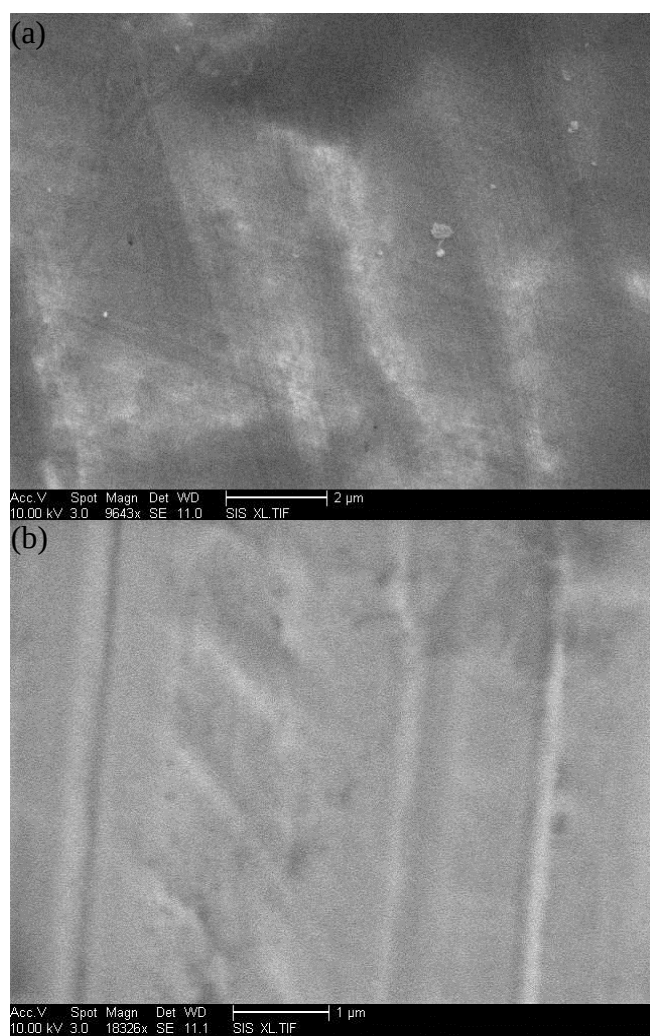


Figure 5.1: SEM images of (a) platinum and (b) nickel substrate surfaces.

5.1 Copper Deposits on Platinum Substrates

Three deposits were done on platinum and analyzed by SEM. Table 5.1 shows the plating conditions for the three samples.

Table 5.1: Plating conditions for copper deposits on a platinum substrate.

Sample	Current Density (mA/cm ²)	Flow Rate (L/min)	Final Charge (C)	Calculated Final Thickness (μm)
P1	10	2.5	64.00	30.0
P2	200	2.5	64.14	30.1
P3	200	7	64.11	30.1

SEM images of the three samples 30 days post-deposition are shown in Figures 5.2-5.4. Samples P1 and P2 had small particles of approximately 100-250 nm in size on top of a smooth underlying deposit, while sample P3 had a very coarse granular structure with approximately 200-250 nm sized grains. X-ray diffraction was used to analyze the samples made on platinum and showed that the samples were pure copper, so the particles seen are not a result of a precipitate or an impurity.

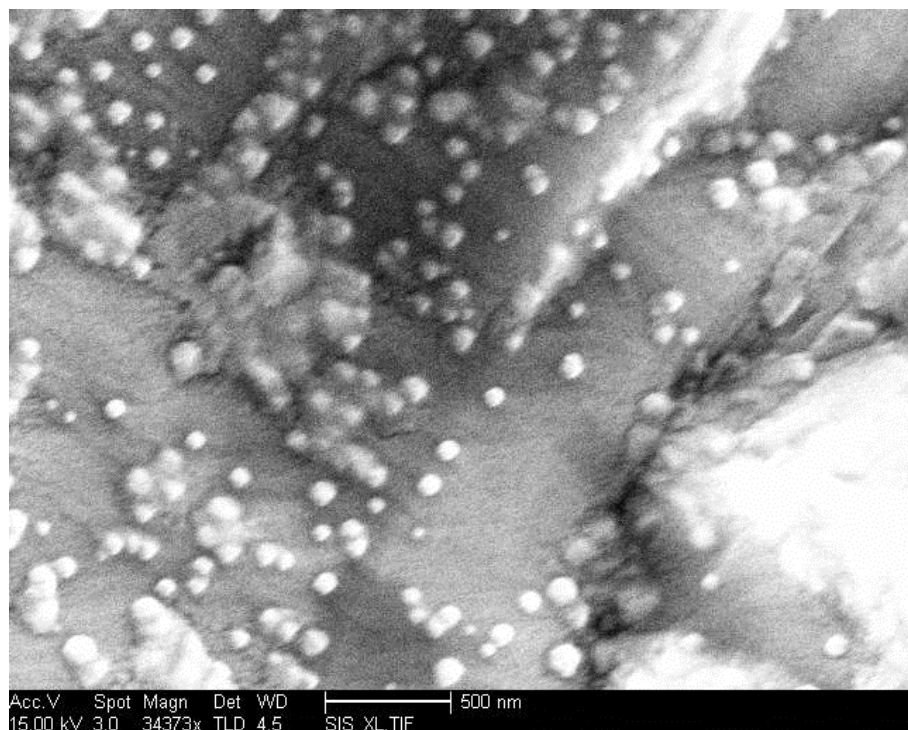


Figure 5.2: SEM image of sample P1 produced at 10 mA/cm² and 2.5 L/min.

Sample P1 shows small roundish particles that are on top of a much larger grained background. This morphology looks similar to SEM images of the nucleation step of copper deposition where the deposition time is so short that the substrate is not covered yet.⁷ It might be that layers are forming and the particles observed are from nucleation of a new layer.

Sample P2 looks similar to sample P1 in that there are larger grains with smaller particles on top. The small particles for sample P2 are larger (100-250 nm) than for P1 (100-150 nm) and more angular. The difference in size and shape of the smaller grains in P2 versus P1 could be due to the difference in current densities during deposition.

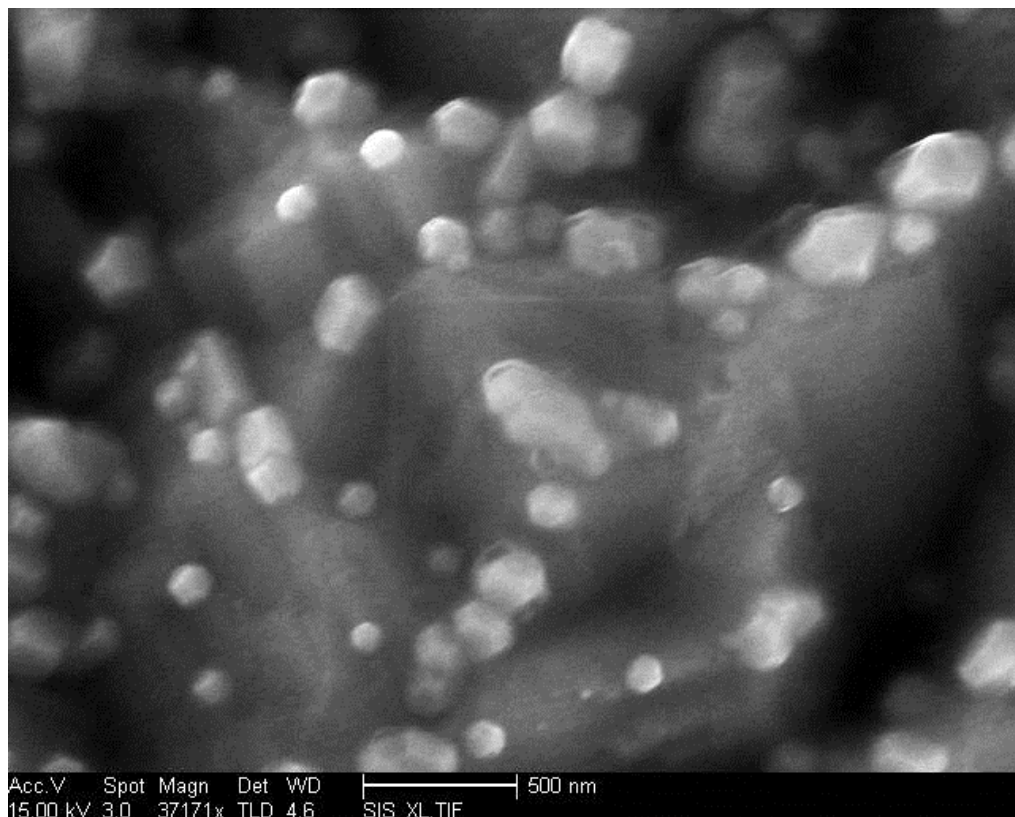


Figure 5.3: SEM image of sample P2 produced with 200 mA/cm^2 and 2.5 L/min .

Sample P3 shows a very different morphology from samples P1 and P2 and is similar to deposits made with high overpotential observed by other methods of electrodeposition⁸ except that the grain sizes are much smaller. It has a very granular structure with most grains being clearly over 100 nm in diameter. While both P2 and P3 were made with a high current density, which is normally associated with the granular morphology seen in sample P3, the difference in morphologies may be due to higher flow rate used for P2. The morphologies seen for these deposits on platinum do not match the reported morphologies of Osborne,⁹ and Sweet¹⁰ for deposits made on copper or Thiemi⁵ on an unknown substrate.

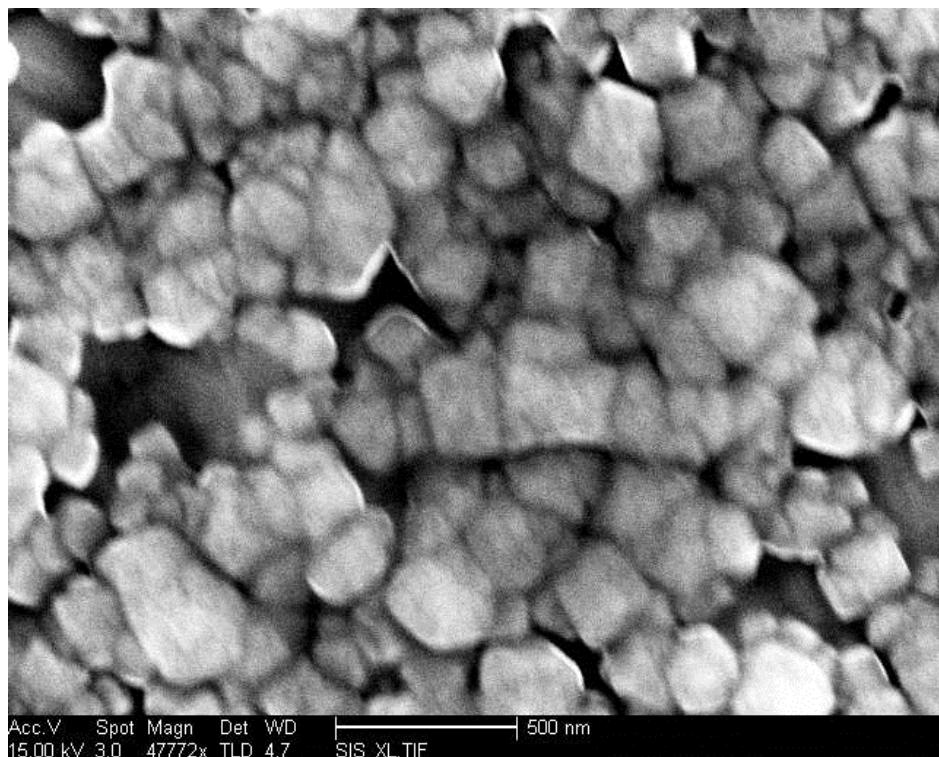


Figure 5.4: SEM image of sample P3 made at 200 mA/cm² and 7 L/min.

5.2 Copper Deposits on Nickel Substrates

Since the copper deposits on platinum did not show the expected morphology or grain size reported in previous work by Thiemi⁵, Osborne⁹ or Sweet¹⁰ copper was plated onto nickel substrates. Table 5.2 shows the plating conditions for the four copper deposits on nickel substrates.

Table 5.2: Plating conditions for copper deposits on nickel substrates.

Sample	Current Density (mA/cm ²)	Flow Rate (L/min)	Final Charge (C)	Calculated Final Thickness (μm)
N1	10	2.5	63.99	30.0
N2	10	7	63.98	30.0
N3	200	2.5	64.04	30.0
N4	200	7	64.25	30.1

5.2.1 Morphology

The morphologies of the four copper samples deposited on nickel showed grains of various shapes. As shown in Figure 5.5, at 15 days post-deposition samples N2, and N3 showed a mix of pyramidal and cuboidal grains that are not connected. Pyramidal grains are most often seen in depositions with slow growth (low current density) and with few impurities.¹¹ While sample N2 was made with low current density, sample N3 was not. It is unclear why sample N2 was similar to N3 when they were made with different current densities; however the difference in flow rate at which they were deposited might be the reason. Sample N1 had oblong grains that while not touching were more closely grouped. The oblong grains were oriented randomly and did not line up with the fluid flow. Sample N4 had polygonal grains with some of them connecting to each other. Polygonal grains are more associated with higher current densities than pyramidal grains and sample N4 was plated with a higher current density. Figure 5.5 shows all four samples at 15 days post-deposition. The copper deposits on nickel showed expected morphologies such as pyramidal,

cuboidal, and polygonal shaped grains¹¹ while also having grain sizes less than 100 nm.

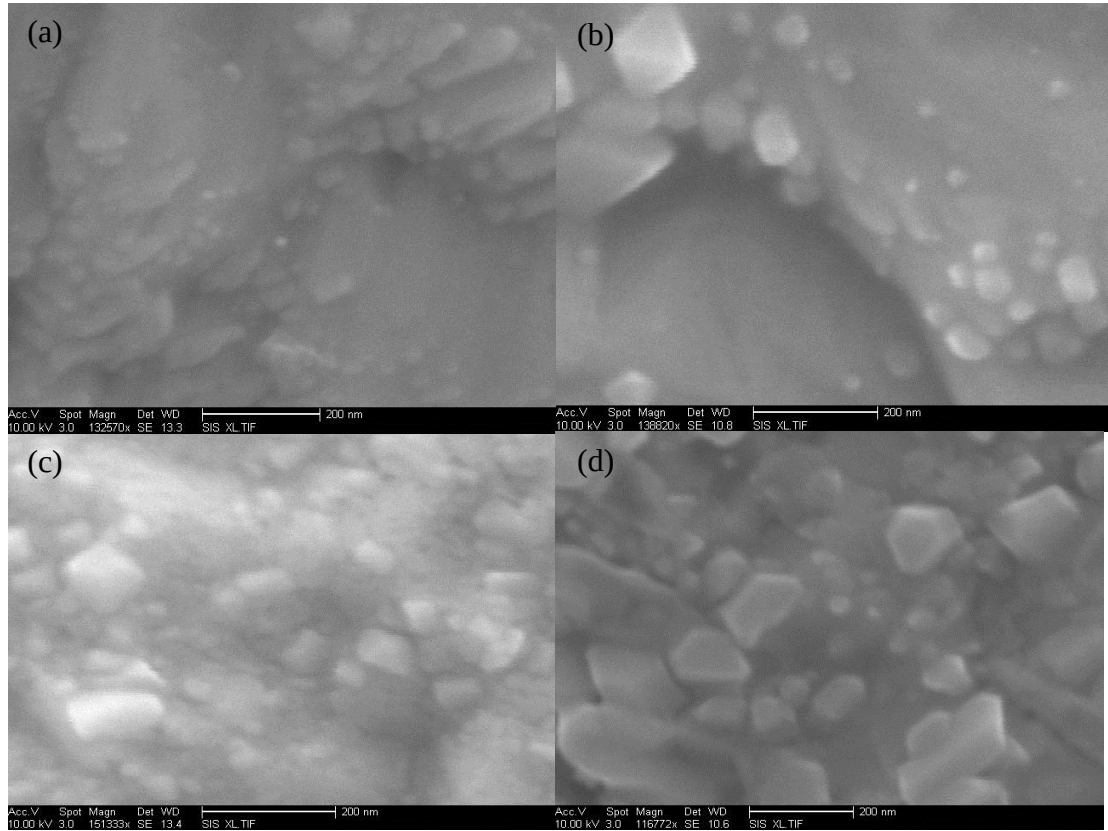


Figure 5.5: SEM images of (a) N1, (b) N2, (c) N3 and (d) N4 at 15 days post-deposition.

5.2.2 Grain Size Distribution

The effects of plating conditions on the size and distribution of grains were examined. Table 5.3 shows the grain size data and Figure 5.6 shows the grain size distribution at 15 days post-deposition. At 15 days post-deposition the samples N1-N3

had approximately the same average grain size, ~45 nm while sample N4 was quite a bit higher at 73 nm.

Table 5.3: Grain size data for samples 15 days post-deposition.

Sample	Minimum (nm)	Maximum (nm)	Average (nm)	Standard Deviation (nm)
N1	19	100	44	22
N2	13	134	49	28
N3	24	114	47	22
N4	32	152	73	35

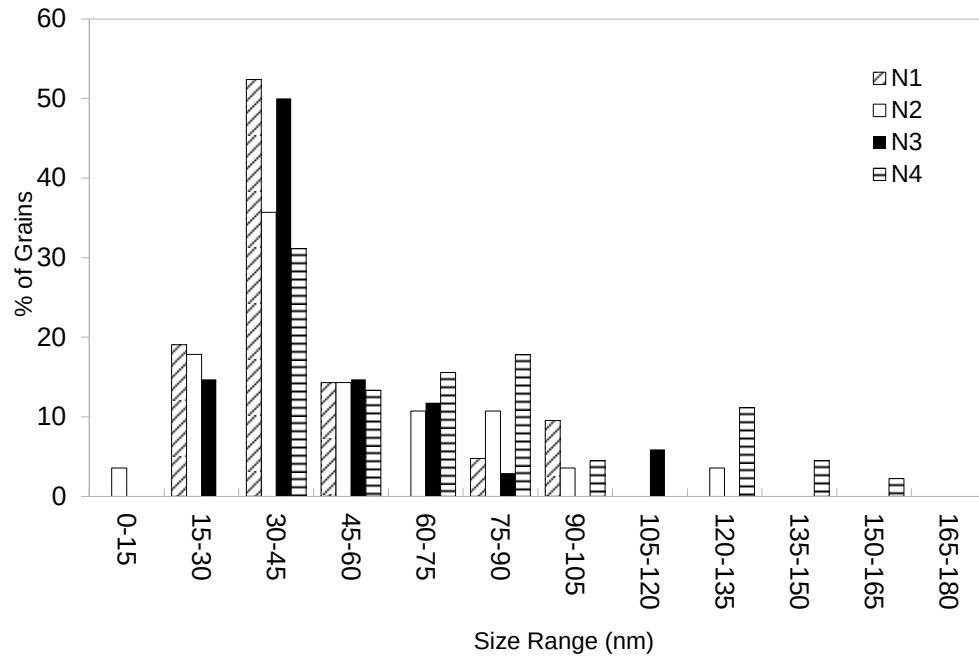


Figure 5.6: Grain size distribution for all samples at 15 days post-deposition.

The data for the deposits 38 days post-deposition are shown in Table 5.4 and Figure 5.7. After 38 days post-deposition sample N1, which was plated with both a low current density and a low flow rate, had the smallest grains, ~ 38 nm. Samples N2

and N3 had similar average grain sizes, ~60 nm while sample N4 had a much higher grain size average than the other samples, ~101 nm.

Table 5.4: Grain size data for samples 38 days post-deposition.

Sample	Minimum (nm)	Maximum (nm)	Average (nm)	Standard Deviation (nm)
N1	10	78	38	17
N2	16	296	63	39
N3	26	155	58	28
N4	83	115	101	11

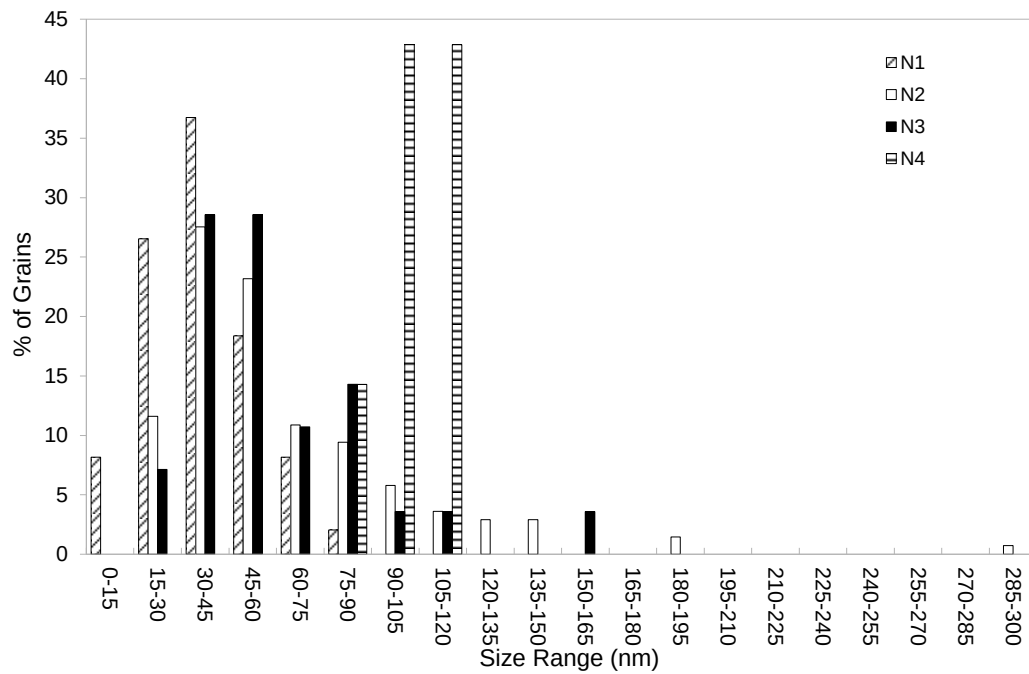


Figure 5.7: Grain size distribution of all samples measured 38 days post-deposition.

Table 5.5 and Figure 5.8 show the data for 230 days post-deposition.

After 230 days the images of samples N1 and N3, deposited with a low flow rate, have almost the same grain size, ~ 33 nm, which is smaller than the average grain sizes for the images taken at 15 and 38 days. This is most likely an anomaly because of the small sample size. Samples N2 and N4, deposited at high flow rate, also have nearly the same grain size, around 112 nm.

Table 5.5: Grain size data for samples 230 days post-deposition.

Sample	Minimum (nm)	Maximum (nm)	Average (nm)	Standard Deviation (nm)
N1	11	106	34	19
N2	37	299	110	62
N3	14	131	33	23
N4	34	289	114	47

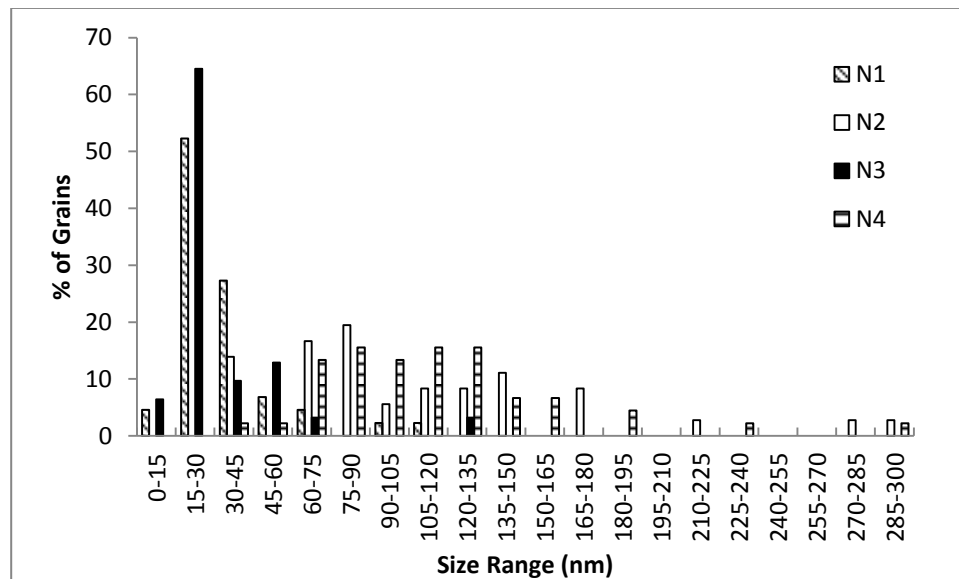


Figure 5.8: Grain size distribution of all samples measured 230 days post-deposition.

The following generalizations can be made. Generally, samples N1 and N3, plated with a low flow rate, had the smallest average grain size and smallest distribution in grain size. When compared with the data from Thiemi⁵ the grain sizes from these experiments were smaller.⁵ Thiemi⁵ showed two samples with average grain sizes of 79 and 68 nm for plating conditions of 2.5 L/min with a current density of either 10 mA/cm² or 75 mA/cm², respectively.⁵ Sample N1 was made at with the same plating conditions as one of Thiemi⁵'s samples, but shows an a grain size of almost half the size. A reason may be that the samples were stored some time before analysis and grain growth may have occurred. Sample N4, deposited with a high flow rate and a high current density, always had the highest average grain size of 73 -114 nm.

Overall these few samples were able to show that it is possible to obtain grain sizes less than 100 nm using an IJE system. It seems that a low flow rate gives the smallest grain sizes and high current density and high flow rate gives the largest grain sizes. While high current density is associated with smaller grain sizes⁵ this was not observed in these experiments. The flow rate seemed to have the most influence over grain size with a lower flow rate giving smaller grain sizes with the IJE system.

5.2.3 Time Dependence of Morphology

The morphology of the samples changes over time for all samples except N3. These changes in morphology could be associated with self-annealing, the growth of grains over time at room temperature, observed for nanograin copper deposits.¹²⁻¹⁴

Figure 5.9 shows the grain structure of sample N1 taken 15, 38 and 230 days post-deposition. Sample N1 has square and oblong grains that lay along the slopes of the larger mountains and valleys in the microstructure. There is a clear change in morphology between the SEM images taken at 15 and 38 days post-deposition. The grains that can be seen after 15 days were less distinct than the grains seen at 38 days post-deposition. There was no appreciable change in morphology observed between the SEM images taken at 38 and 230 days post-deposition.

The SEM images of sample N2 at 15, 38 and 230 days post-deposition are shown in Figure 5.10. For sample N2 the SEM images show a changing morphology where the grains change in shape and number as time progressed. At 15 days post-deposition there were only a few grains and most of them were square-like. At 38 days post-deposition there was a greater number of grains and they had become pyramidal in shape. After 230 days the grains were for the most part interconnected and hexagonal in shape.

Figure 5.11 shows SEM images of sample N3 taken 15, 38 and 230 days post-deposition. For sample N3 the grains are pyramidal and cubic in shape and are not interconnected. The SEM images of sample N3 show little evidence of a changing morphology.

The SEM images of sample N4 taken 15, 38 and 230 days post-deposition are shown in Figure 5.12. Sample N4 shows similar morphology and growth to sample N3. There is not a significant difference in number of grains between the SEM images taken at 15 and 38 days, but the particles are flatter at 15 days post-deposition

compared to 38 days. At 230 days post-deposition the grains are interconnected and on top of each other.

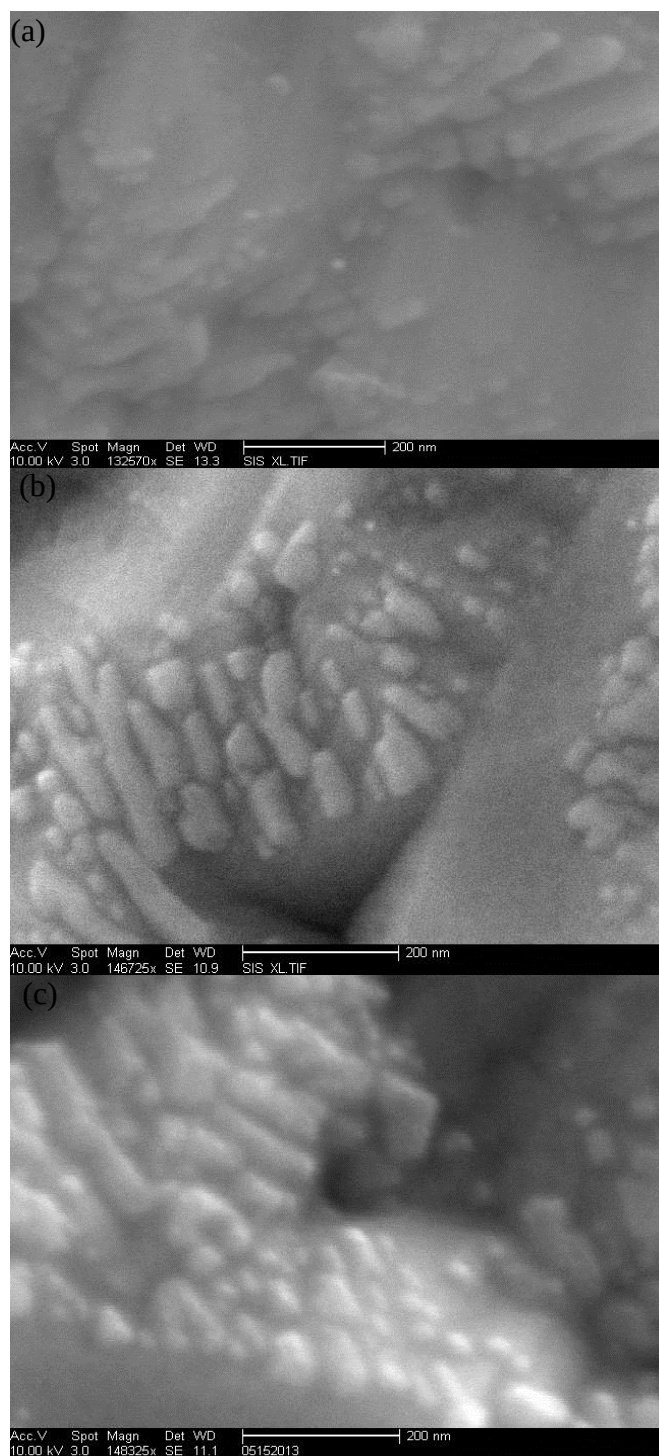


Figure 5.9: SEM of sample N1 produced at 10 mA/cm^2 and 2.5 L/min at (a) 15, (b) 38 and (c) 230 days post-deposition.

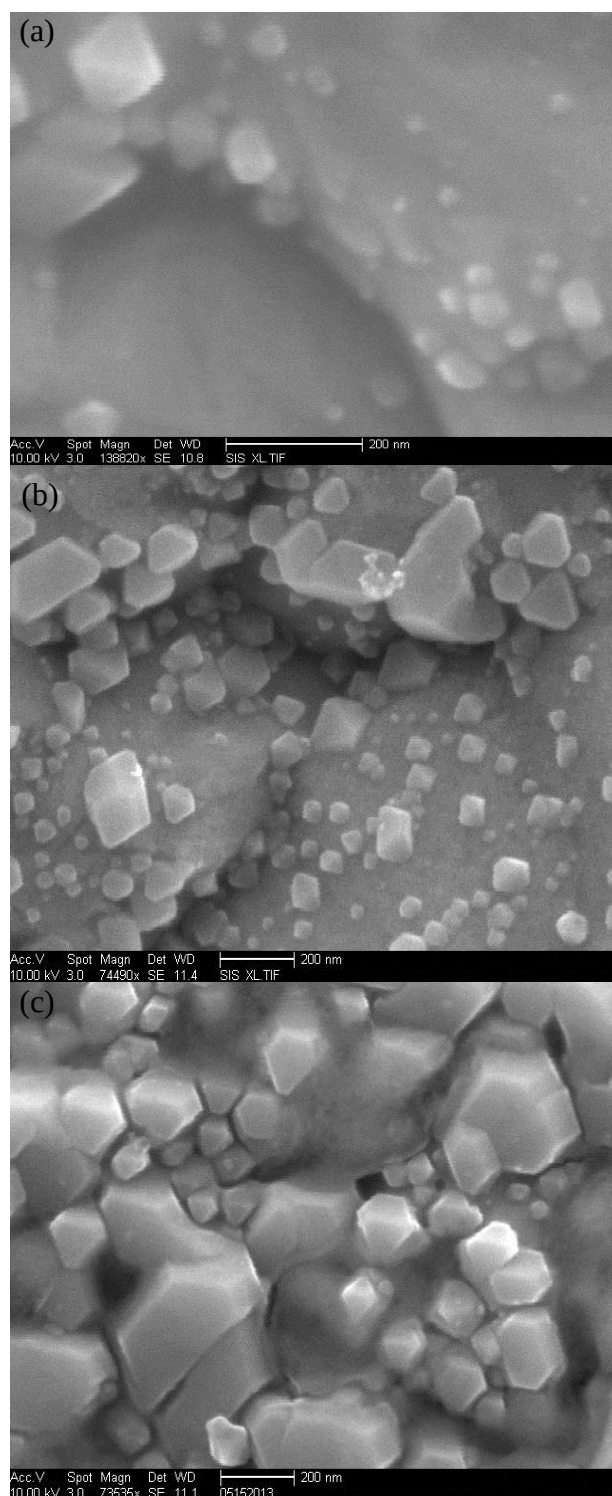


Figure 5.10: SEM of sample N2 produced at 10 mA/cm^2 and 7 L/min at (a) 15, (b) 38 and (c) 230 days post-deposition.

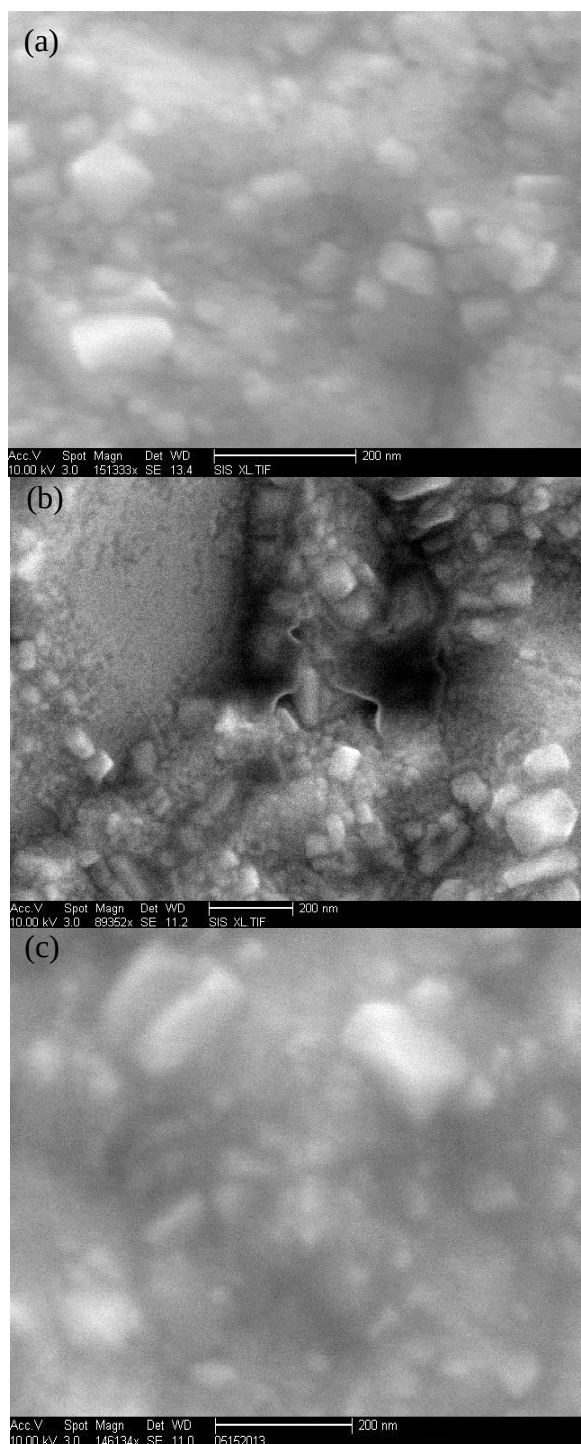


Figure 5.11: SEM of sample N3 produced at 200 mA/cm^2 and 2.5 L/min (a) 15, (b) 38 and (c) 230 days post-deposition.

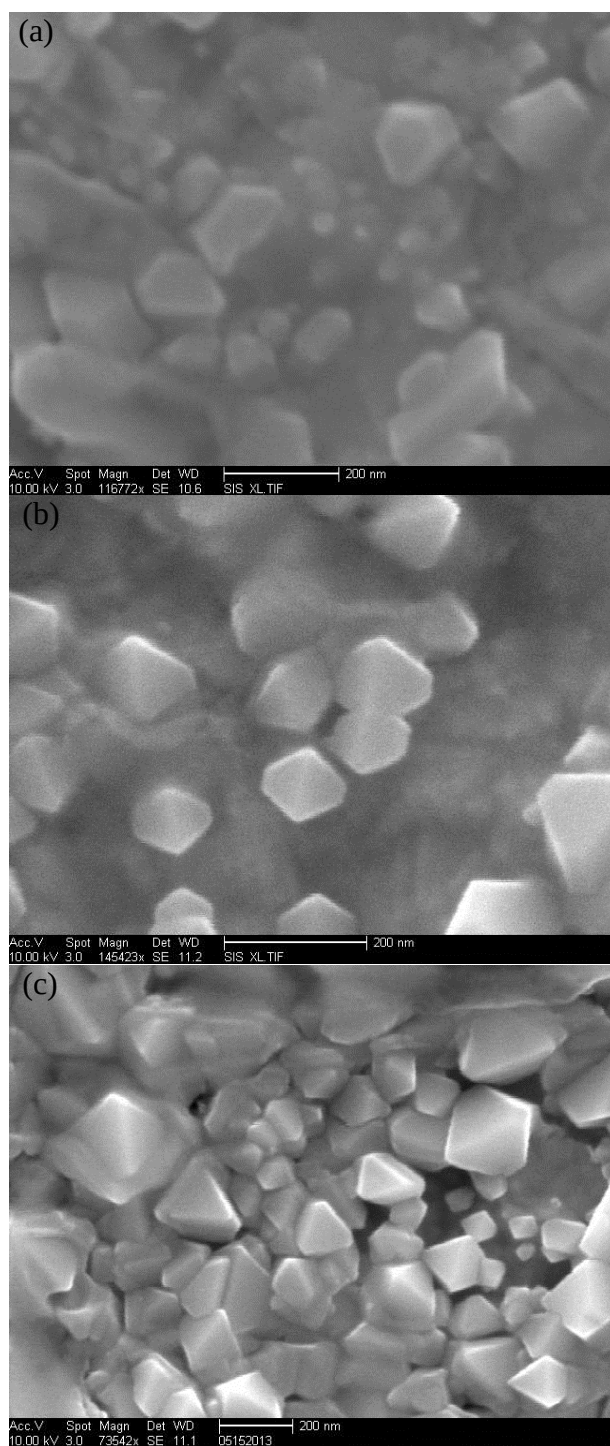


Figure 5.12: SEM of sample N4 produced at 200 mA/cm^2 and 7 L/min at (a) 15, (b) 38 and (c) 230 days post-deposition.

5.2.4 Time Dependence of Grain Size

It was difficult to analyze grain growth, as only one SEM image of the deposit was used to calculate the grain size. However, it is clear that at least for the samples plated at a high flow rate, N2 and N4, there was substantial growth that occurred between 38 and 230 days post-deposition.

Table 5.6 shows the grain size data and Figure 5.13 shows the grain size distribution for sample N1. Sample N1 showed the grain size becoming smaller as time progressed. But since the standard deviations are large, the variation in grain size is most likely little or none. From Figure 5.13 the general size and distributions are similar for each time frame. This seems to agree with the lack of changes in morphology observed.

Table 5.6: Grain size data of sample N1 over time.

	Minimum (nm)	Maximum (nm)	Average (nm)	Standard Deviation (nm)
15 Days	19	100	44	22
38 Days	10	78	38	17
230 Days	11	106	34	19

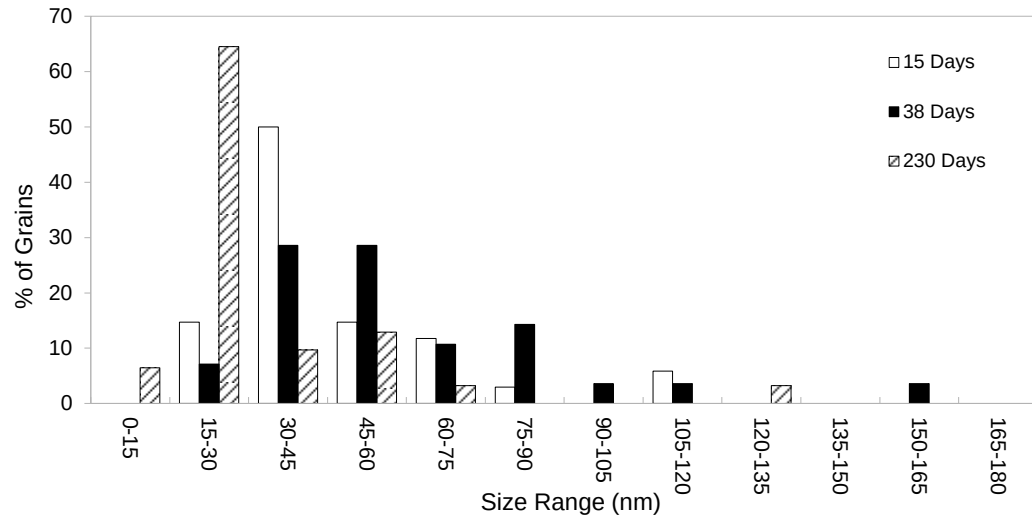


Figure 5.13: Grain size distribution of sample N1 at 15, 38 and 230 days post-deposition.

In agreement with the change in morphology seen, sample N2 shows grain growth over time as shown in Table 5.7. Figure 5.14 shows the grain size distribution over time shifting to higher values as one would expect if the small grains are being cannibalized by the bigger ones as in self-annealing.¹ By taking the measurements at 15 days post-deposition as $t = 0$ it was possible to fit the data to equation 2.1 for the grain growth of sample N2 as shown in Figure 5.15. For $n = 1$ a linear regression gave $k = 45$ and an R^2 value of 0.99.

Table 5.7: Grain size data for sample N2 over time.

	Minimum (nm)	Maximum (nm)	Average (nm)	Standard Deviation (nm)
15 Days	13	134	49	28
38 Days	16	296	63	39
230 Days	37	299	110	62

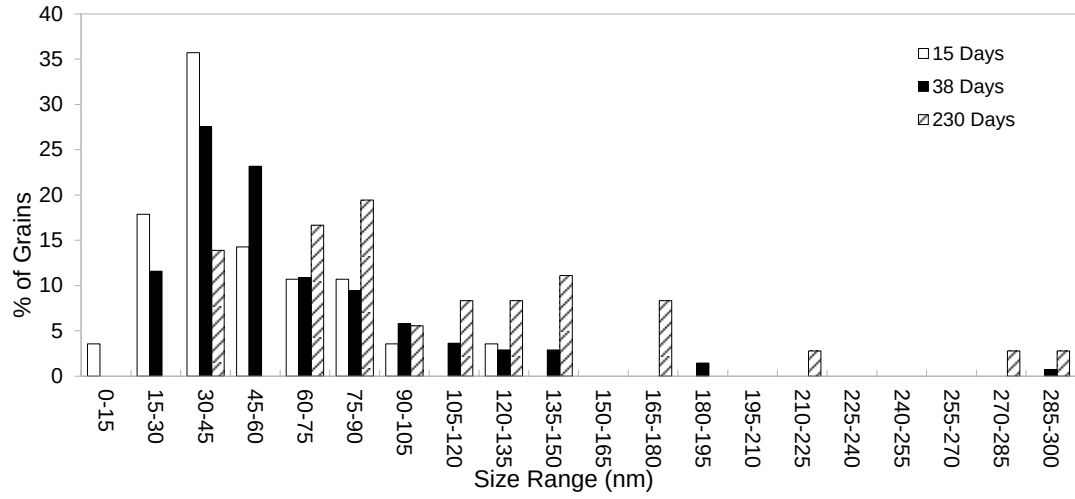


Figure 5.14: Grain size distribution of sample N2 at 15, 38 and 230 days post-deposition.

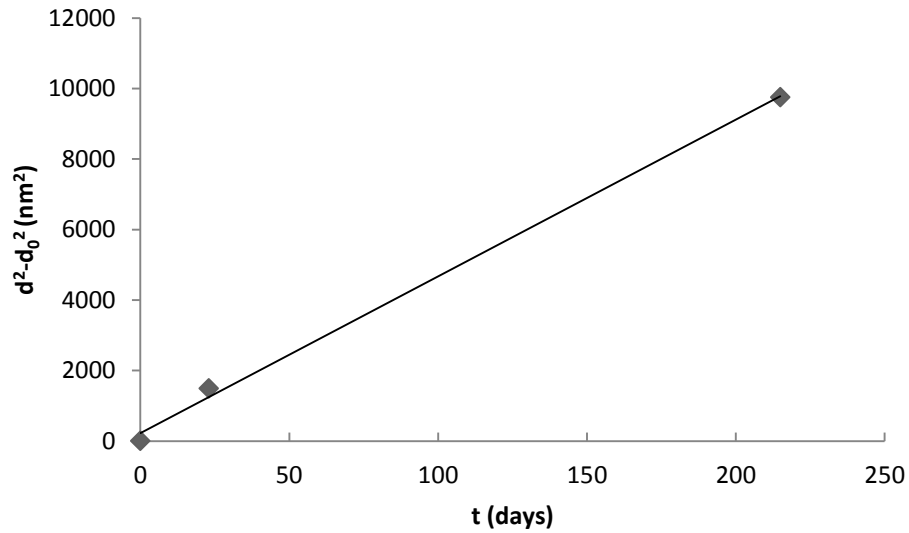


Figure 5.15: Fit of Equation 2.1 for sample N2 with $t = 0$ at 15 days post-deposition.

The grain size data for sample N3 is shown in Table 5.8. For sample N3 the average grain size increases, then decreases with time, but like sample N1 the values are close together with a large standard deviation, so it is likely that little or no grain growth occurred. Figure 5.16 shows the grain size distribution over time and it also shows little if any growth. While the change in morphology of sample N3 suggested self-annealing might have occurred between 15 and 38 days, this is not supported by the grain size data.

	Minimum (nm)	Maximum (nm)	Average (nm)	Standard Deviation (nm)
15 Days	24	114	47	22
38 Days	26	155	58	28
230 Days	14	131	33	23

Table 5.8: Grain size data for sample N3 over time.

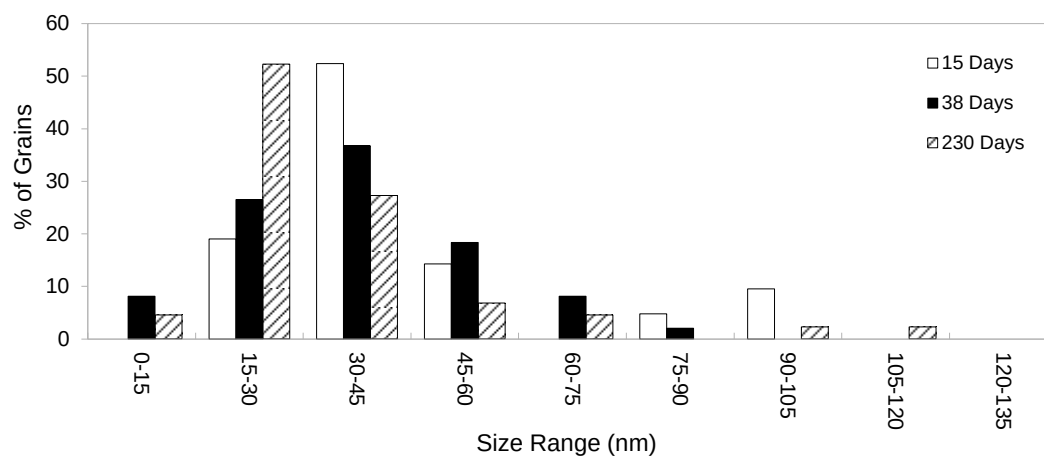


Figure 5.16: Grain size distribution of sample N3 at 15, 38 and 230 days post deposition.

Similar to sample N2, sample N4 showed grain growth over time as shown in Table 5.9. Figure 5.17 shows the same shifting of grain size distribution as sample N2 indicating self-annealing, which matches with the morphology changes seen for sample N4. Unlike for sample N2, the grain growth for sample N4 did not fit equation 2.1 ($k = 38$, $R^2 = 0.44$) as shown in Figure 5.18. The average grain size at 230 days has a very large standard deviation which might account for the deviation from the standard growth curve.

Table 5.9: Grain size data for sample N4 over time.

	Minimum (nm)	Maximum (nm)	Average (nm)	Standard Deviation (nm)
15 Days	32	152	73	35
38 Days	83	115	101	11
230 Days	34	289	114	47

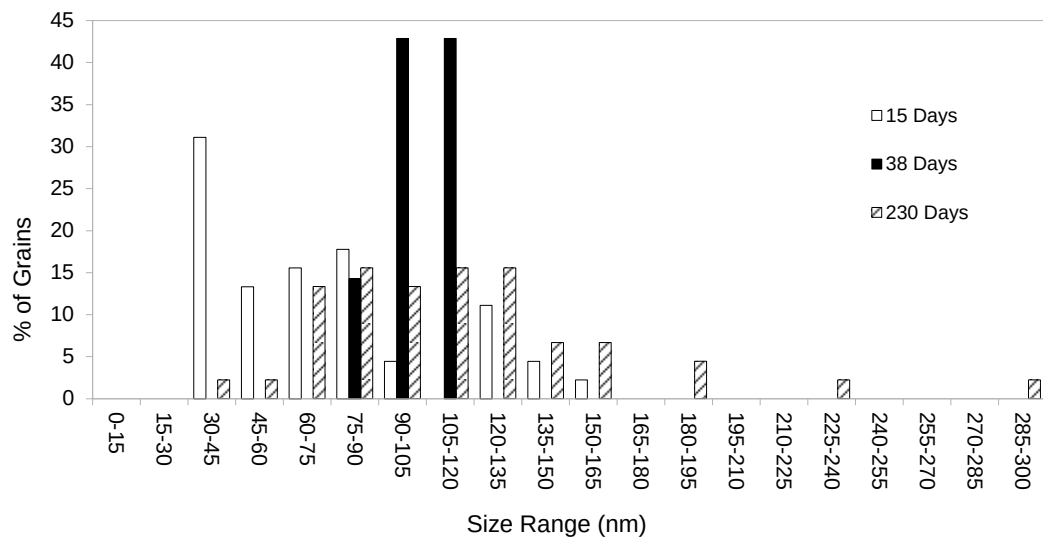


Figure 5.17: Grain size distribution of sample N4 at 15, 38 and 230 days post-deposition.

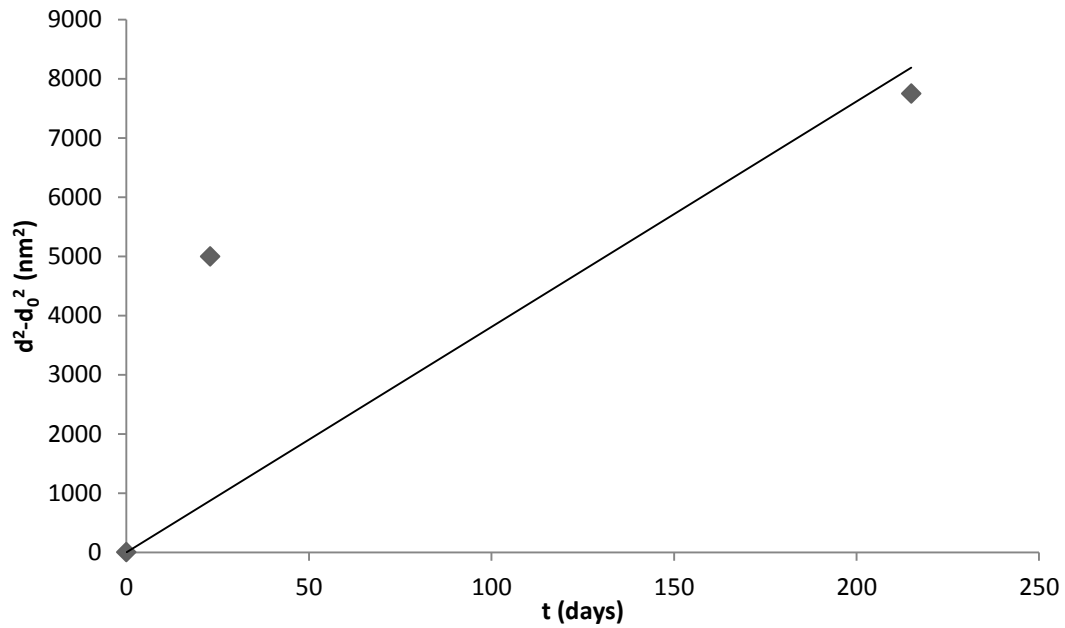


Figure 5.18: Fit of Equation 2.1 of sample N4 with $t = 0$ at 15 days post-deposition.

According to Harper the time it takes for grain growth to occur is roughly equal for all deposits with a deposit thickness greater than $1\text{ }\mu\text{m}$.¹² This was not seen with this data as all samples were the same thickness yet had different grain growth times. Using the 15 days as the time to stop growing for samples N1 and N3 and 230 days for samples N2 and N4 the k value was computed according to equation 2.2 using Harper's given values of $0.23\text{ }\mu\text{m}$ for d_0 and 5.5 hr for t_0 .¹² Samples N1 and N3 had a k value of 6 while samples N2 and N4 had a k value of 92 compared to Harper's value of 2.5.¹² While some of the error comes from not knowing the precise time that grain growth stopped, it is also clear with such different k values for deposits with the same thickness that these samples do not follow Harper's grain growth model.

It is likely the changes in morphology and grain size observed are associated with self-annealing. Since all samples were deposited with the same plating bath and are the same thickness, the only variable studied that affects the self-annealing time was plating rate.^{1,12,13}

Sample N1 shows morphology changes only between 15 and 38 days post-deposition, which suggests self-annealing ended within that time frame. This does not agree with the grain size data, but this could be because of the small sampling of grain size. Sample N2 followed the basic grain growth model, equation 2.1, which agrees with previous findings on self-annealing when no additives were in the plating solution.¹⁴ Since sample N3 shows little evidence of morphology change or grain growth that indicates that any self-annealing was completed before 15 days or that no self-annealing took place. Samples N2 and N4, which showed morphology and grain size changes after 230 days after deposition, could either have stopped self-annealing between 38 and 230 days or self-annealing could have continued past 230 days. Both of these scenarios are consistent with observations that grain growth from self-annealing can last for months.¹

Overall, the changes in morphology and grain size showing self-annealing do not match the predictions from literature that samples made at higher current densities self-anneal faster.¹ The samples made with the high current density, N3 and N4, do not show the same behavior and N4 self-annealed for a longer time than N2 which was made at a lower current density. The IJE system is different from other systems, including DC and pulse plating, used to create nanograin copper in that the fluid flow

is controlled and the fluid impinges on the substrate. This could account for the differences between these findings and literature.

5.3 References

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6. Conclusions

The principle objective of this research was to determine the plating conditions of the unsubmerged impinging jet electrode system that produced nanograin copper deposits and how those deposits changed over time. Specifically, the variables that were investigated were current density, flow rate and substrate type. The deposition conditions that were used were at the limits of operation of the IJE system: a current density of either 10 or 200 mA/cm² and a flow rate of 2.5 or 7 L/min. The plating solution that was used for all experiments was an acid copper sulfate bath of 1 M and a pH of 1.5.

The copper deposits on platinum showed grain sizes larger than 100 nm and morphologies of either cauliflower-like grains associated with high current density or small spherical grains that looked like the very beginnings of grain growth. Since the deposits on platinum did not give the anticipated grain size of less than 100 nm, deposits were made on nickel substrates.

The copper deposits on nickel showed morphologies of pyramidal, cuboidal, elongated and polygonal grains. Grain sizes ranged from 44 to 73 nm at 15 days post-deposition. The smallest grains occurred for samples made with a low flow rate, while a high flow rate was associated with larger grains. Contrary to literature² that used other plating systems, a higher current density did not produce smaller grain size. Even with only four samples this suggests that flow rate has a greater impact on grain size than current density in an IJE system.

The deposits made on nickel were imaged by SEM at 15, 38 and 230 days post-deposition to study grain growth at room temperature, called self-annealing. The samples produced with low flow rates, N1 and N2, showed little or no evidence of self-annealing. Samples N3 and N4 plated with high flow rate showed evidence of self-annealing and the grains were still small at approximately 112 nm in size 230 days post-deposition.

6.1 References

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7. Future Work

To make the IJE system a viable means to create nanograin deposits on a large scale more work on the effects of processing conditions on the grain size and morphology as well as any self-annealing behavior should be conducted. Since additives such as brighteners and levelers are commonly used for electroplating copper on microelectronics the effects of additives on the grain size with the IJE system should be studied. Since alloys and nickel deposits are also being investigated as possible materials in the electronics industry experiments using the IJE system to deposit these materials would be beneficial.

To study the self-annealing behavior of the deposits in more detail, measurements could be made directly after deposition and at constant intervals until no further change in grain size is seen. Also x-ray diffraction could be used to measure the average grain size of the nanograins and the planar orientation of grains.