Electrodeposition of nickel-copper alloys and nickel-copper-alumina nanocomposites into deep recesses for MEMS

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ELECTRODEPOSITION OF NICKEL–COPPER ALLOYS AND NICKEL-COPPER-ALUMINA NANOCOMPOSITES INTO DEEP RECESSES FOR MEMS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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Doctor of Philosophy

in

The Department of Chemical Engineering

By
Amrit Panda
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To Shwetha...
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# TABLE OF CONTENTS

DEDICATION........................................................................................................... ii

ACKNOWLEDGEMENTS.......................................................................................... iii

ABSTRACT................................................................................................................ vi

CHAPTER 1. INTRODUCTION..................................................................................... 1

CHAPTER 2. LITERATURE REVIEW.......................................................................... 6
  2.1 Ni-Cu Alloy Electrodeposition................................................................. 7
  2.2 Composite Electrodeposition................................................................. 15
  2.3 Electrodeposition in Recessed Geometries............................................. 27
  2.4 Composite Deposition in Recesses......................................................... 30
  2.5 LIGA Microdevices................................................................................... 31
  2.6 Materials for LIGA................................................................................... 35

CHAPTER 3. EXPERIMENTAL DESIGN................................................................. 37
  3.1 Recessed Electrode..................................................................................... 38
    3.1.1 Substrate Preparation......................................................................... 38
    3.1.2 Bonding............................................................................................... 38
    3.1.3 Lithography of PMMA......................................................................... 39
    3.1.4 Development and Rinsing................................................................... 40
    3.1.5 Etching................................................................................................. 43
  3.2 Holder Design............................................................................................. 44
  3.3 Plating Cell Setup....................................................................................... 46
  3.4 Rotating Cylinder Electrode........................................................................ 47
  3.5 Instrumentation.......................................................................................... 49
  3.6 Electrolytes................................................................................................ 49
  3.7 Characterization........................................................................................ 50

CHAPTER 4. EXPERIMENTAL RESULTS............................................................ 52
  4.1 Deep Recess Deposition............................................................................. 52
    4.1.1 Pulse Parameter Selection.................................................................. 53
    4.1.2 Impedance Spectroscopy..................................................................... 58
    4.1.3 Ni-Cu Alloy Deposition....................................................................... 61
      4.1.3.1 Low pH Deposition....................................................................... 61
      4.1.3.2 High pH Deposition....................................................................... 65
    4.1.4 Ni-Cu-γ-Al2O3 Composite Deposition............................................... 70
      4.1.4.1 Effect of pH.................................................................................... 70
      4.1.4.2 Effect of Applied Current Density................................................. 80
      4.1.4.3 Effect of Alumina Concentration.................................................. 85
    4.1.5 Growth Rates....................................................................................... 88
  4.2 RCE Deposition........................................................................................... 90
ABSTRACT

Electrodeposition is an important component in the fabrication of micro electro mechanical systems (MEMS). Nickel is the most commonly used material to produce three dimensional microstructures and few material alternatives have been demonstrated. In this dissertation, electrodeposited Ni-Cu alloys and nanocomposites are investigated as possible replacements for nickel in microsystems. Ni-Cu alloys are attractive for their corrosion resistance, magnetic and thermophysical properties. Alumina nanoparticulates included into metal matrices improve hardness and tribology of deposits. The Ni-Cu alloys and Ni-Cu-γ-Al₂O₃ nanocomposites were electrodeposited from a citrate electrolyte, both at low and high pH. Electrodeposition experiments were performed in recessed microelectrodes 500 µm thick and also on rotating cylinder electrodes. Recessed electrodes were produced by x-ray synchrotron radiation at the Center for Advanced Microstructures and Devices (CAMD). The concentration of copper in the electrolyte was much lower than the nickel concentration to ensure diffusional control. In the microstructure, the copper concentration in the deposit increased along the height, leading to a graded microstructure. This is indicative of a changing boundary layer and a transient process. The addition of alumina nanoparticles in the electrolyte led to an enhancement of copper concentration in the deposit, resulting from an enhancement of its mass transport rate. Two numerical models were developed to describe the steady state and non-steady state deposition processes. The effect of alumina on the metal deposition partial currents and side reactions is simulated by using a surface coverage model. Rotating cylinder experiments and simulation are used to extract kinetic and diffusional parameters of the nickel and
copper species. On the recessed electrodes a transient model taking into account the
time dependence of concentration is developed. The rise of surface pH, concentration
gradients and buffering effects of the complexing agents are explained by the non-
steady state model.
CHAPTER 1.

INTRODUCTION

Electrodeposition or electroplating is the process by which an applied current or potential is used to deposit a film of metal or alloy by the reduction of metallic ions onto a conductive substrate. The electrodeposition of particulates along with a metal or alloy leads to the formation of a composite. Electroplating finds numerous applications as thin films and as three-dimensional, thick structures in microdevices. The properties of interest for both thick and thin films cover a broad range, including corrosion resistance, wear resistance, thermal, magnetic and optical characteristics. Applications include materials for printed-wiring boards, contacts, connectors, and magnetic-recording heads.\textsuperscript{1,2} High-resolution lithographic techniques has enabled electronic device integration, with electrodeposits several hundred microns thick. The importance of electrodeposition as a fabrication technology in the microelectronics industry is growing. For some of the fabrication processes involved, electrodeposition offers advantages over competing technologies such as physical and chemical vapor deposition, in that it requires simpler instrumentation and operating conditions.\textsuperscript{3} With the trend toward miniaturization, electrodeposition has established itself as the manufacturing technology of choice.\textsuperscript{1,4} Electrodeposition also holds great promise to conformably deposit metals and alloys for microelectronic fabrication and HARMs (High Aspect Ratio Microdevices).

Fabrication of high aspect ratio microstructures by electrodeposition is of increasing interest for a multitude of applications in microelectromechanical systems (MEMS). Conventional anisotropic silicon etching used to create recesses for
subsequent metal deposition is restricted to crystallographic orientations. Traditional ultraviolet (UV) lithography is limited by the depth of the pattern as a result of the lower energy of the UV beams, resist sensitivity and contrast.\textsuperscript{5} To produce tall, three dimensional structures, deep x-ray lithography, which uses high energy x-rays produced by a synchrotron, is utilized to transfer a pattern onto thick x-ray resists with lateral dimensions on the order of a few microns and with heights of up to 2 mm. Lithography comprises one step of the LIGA process. LIGA is the German abbreviation of the three major process steps, lithography (Lithographie), electroplating (Galvanoformung) and molding (Abformung).\textsuperscript{6} The use of the LIGA process overcomes many drawbacks of other traditional fabrication methods and pattern transfer techniques such as chemical etching, sputter etching, reactive ion etching. Electrodeposition is an integral part of the LIGA process. It is employed after exposure and development of the resist and is used to build up a complementary pattern onto a metal substrate by filling the empty spaces of the electrically non-conductive resist starting from the electrically conducting base. The metal pattern produced in such a way can then be used as the microdevice itself or can serve as a mold for plastic replication.\textsuperscript{7} X-ray lithography combined with electroforming and molding techniques thus allow the fabrication of microstructures, several hundred micrometers in depth, with any cross sectional shape with nearly atomic resolution and vertical side-walls.\textsuperscript{5}

Applications of LIGA microstructures are in the manufacture of a wide variety of devices, including microelectronic circuits, sensors, actuators and microoptical microstructures. Several prototypes of micro heat-exchangers, microturbines with partly
movable parts, micropumps with valve openings and a pumping chamber have also been demonstrated.²

Electrodeposited elemental nickel has been the material of choice to demonstrate a variety of microdevice prototypes, including micro-gears, and micro-cantilevers.⁶ Ehrfeld et al.⁸ have reviewed several elemental deposition systems such as Ni, Cu, Au, Fe and also a few alloy systems like NiFe and NiCo for their suitability in the fabrication of HARMs. At present, materials electroformed as LIGA microstructures and devices are limited to only a few elemental metals and alloys such as Ni, Cu, Au, Zn, Ni-Co, and Ni-Fe etc. A paucity of available materials limits the utilization of LIGA products in a number of potential applications where materials, with specifically better properties such as corrosion resistance and mechanical strength are required. A much wider selection of materials with properties that can be tailored to a specific application have to be developed to provide improved and novel applications for future microdevices.

Electrodeposited alloys and composites are of particular interest because of their unique and often superior properties compared with their metal counterparts.³, 19, 64 As thin films, the electrodeposited alloys of nickel have been of interest for their various properties such as low internal stress,⁹ magnetic properties,¹⁰ hardness,¹¹ malleability, ductility¹² and resistance to corrosion.¹³ Nickel copper alloys have great potential in industrial applications where, resistance to corrosion,⁷ and thermo-electric characteristics are required.¹¹ Its corrosion resistance makes it suitable for use as a protective coating in marine and corrosive environments.⁹ Past studies on Ni-Cu alloys have involved work primarily on planar¹⁴-²⁵ electrodes. Relatively few studies exist on
the electrodeposition of copper nickel alloys into recesses, greater than a hundred microns and none completely characterize the deposition process.

Metal composites are pragmatic choices for tailoring the material to a desired property. For example, SiC has been electrodeposited with Ni from a sulfamate electrolyte for MEMS applications.\textsuperscript{92} Several reviews\textsuperscript{43-52} on composite electrodeposition onto unrecessed substrates describe the diverse composite types produced and the many parameters that influence the particle incorporation rate. Properties of composites such as wear resistance\textsuperscript{11} and hardness\textsuperscript{12, 13} were found to be better. Particles in the nanometric range can extend the use of composites for microdevice fabrication. Since microdevices are inherently on the order of micrometers then the composite material that these devices are created from must contain particles that are at least an order of magnitude smaller, nanometric. Even on unrecessed electrodes, few studies have confronted an alloy-composite system and the effect of particles on the metal deposition rate. None, have been concerned with this issue in deep recess plating.

The subject of this dissertation is the deposition of nickel-copper alloys and nickel-copper-alumina nanocomposites into highly recessed electrodes made by x-ray lithography. The deposition of these alloys and nanocomposites onto rotating cylinder electrodes are also studied and used to explain the deposition in the recesses. Often in alloy electrodeposition the deposition rate of the more noble metal is diffusion controlled. Therefore, the control of the deposit composition in the recess becomes a transient problem and complicates the electrodeposition behavior. Two mathematical models – a steady state model and a non-steady state model, are developed to explain
the alloy and composite deposition. The steady state model is used for the deposition on rotating cylinders and predicts the alloy composition and plating efficiency. The non-steady state model is used to understand and explain the deposition process in deep recesses and parameters critical to the plating process are addressed.

The properties of deposits depend on a number of factors such as composition and metallurgical structure (grain size, growth orientation), which are in turn affected by the deposition conditions. These parameters include current density, electrolyte composition, pH and temperature. Local control of these factors is essential for the successful electrodeposition of high aspect ratio geometries with well-defined properties. An improved understanding of alloy and composite codeposition will help to identify the right process conditions to produce high quality microstructures and devices. This introduction is followed by chapters on a survey of relevant literature, the experimental setup, experimental results, model development, and a chapter on discussions and recommendations.
CHAPTER 2.

LITERATURE SURVEY

This chapter contains a review of literature pertinent to the deposition of nickel-copper alloys, metal and composites, electroplated microstructures and different models used to explain the mechanism of electrodeposition. Several electroplating solutions exist for the deposition of nickel-copper alloys and composites, as thin films. For deep recess plating, it is necessary to employ an electrolyte, which offers high current efficiencies, morphologically smooth deposits, the desired composition of deposit, and having the desired properties for the corresponding application, which is dependent on the deposit composition, crystallographic orientation, and grain size. On unrecessed geometries, different approaches – Galvanostatic,\textsuperscript{24} potentiostatic,\textsuperscript{25} pulsed current\textsuperscript{33} and pulse-reverse current deposition,\textsuperscript{71,81} have been used. Important parameters include the concentration of the metallic species in the electrolyte, complexing agents, pH, agitation, applied current density and temperature. Even though numerous literature studies exists on the deposition in unrecessed electrodes, very few studies demonstrate the electrodeposition of any alloys into recesses greater than a hundred microns and are all empirical in nature.

In this chapter, a review of papers dealing with nickel-copper deposition is introduced, followed by a review of composite electrodeposition, electrodeposition into lithographically patterned electrodes, and a review of microdevices fabricated using the LIGA process.
2.1 Ni-Cu Alloy Deposition

Electrodeposition of Ni-Cu alloys has been carried out from a wide variety of baths since the early nineteenth century onto unrecessed substrates. Despite a great deal of research on Ni-Cu alloys, no rigorous studies have been made on their electrodeposition in high aspect ratio recesses. Electrodeposition of these alloys has been demonstrated from a variety of electrolytes such as cyanide,\(^{14}\) citrate,\(^{15}\) sulfamate,\(^{16}\) sulfate-oxalate,\(^{17}\) and pyrophosphate.\(^{18}\) The standard reduction potentials for copper and nickel are +0.34 V and –0.25 V vs. a normal hydrogen electrode (NHE), respectively. The Ni-Cu alloy plating process is classified as a normal codeposition type,\(^{3}\) since the more noble metal, in this case, copper, deposits preferentially, followed by Ni. The standard reduction potentials of Ni and Cu are quite disparate. A complexing agent such as citrate acts to decrease the gap in the reduction potentials between the two metal reactions. It also leads to smoother microstructures.

In 1959 Priscott\(^{15}\) studied the dependence of the composition of the deposit on the cathodic current density, temperature and agitation of the solution. He found a strong dependence between the composition and the cathodic current density. The cathodic current efficiency dropped as the pH was lowered. The effect of increase in temperature was to increase the current efficiency, but did not affect the composition of the deposit. Agitation of the solution increased the Cu content of the deposits. The metal distribution was found to be uniform and the hardness was greater than that of elemental Ni deposited from a Watts bath.
In 1963, Brenner\textsuperscript{26} found that of all the electrolytes studied, citrate electrolytes appeared to show the most promise because they could be used to electrodeposit Ni rich alloys at high current efficiencies. It’s inherently low toxicity, also makes it particularly attractive. In 1989, A. R. Despic\textsuperscript{27} studied the role of the citrate ion and found that it acted as a leveling agent. In a study done by Ishikawa \textit{et al.}\textsuperscript{28} in 1995, the citrate ion was found to act as a brightening agent. In 1996, M. Pushpavanam \textit{et al.}\textsuperscript{29} discovered that citrate ion also acted as a buffering agent. All of the above characteristics make a citrate solution favorable because, it eliminates the need for addition of additives to the bath.

In 1982, Roos \textit{et al.}\textsuperscript{10} carried out the electrodeposition of Cu-Ni alloys from citrate electrolytes, onto rotating electrodes and hull cell electrodes. A rotating disc was found to produce non-uniform current distribution and as a result, a rotating cylinder was recommended. They successfully demonstrated the deposition of nickel-copper alloys where copper was under limiting current. By varying the convective flow and bath composition, a wide variety of compositions of the alloy were obtained. Hull cell experiments also yielded a wide range of surface finishes over a wide range of deposition currents. The citrate was found to act as a brightening agent.

Quang \textit{et al.}, \textsuperscript{9} in 1985 found that sound coherent deposits of Ni-Cu alloy with low internal stress and a wide range of compositions could be achieved from the citrate baths. A thickness greater than 100 microns of a bulk deposit was obtained without cracking. The corrosion resistance of 30 % Cu was as good as metallurgically prepared Monel alloy. Addition of sodium citrate improved the quality of Ni deposited and also the potential stability. They proposed a mechanism for the reduction of Cu in
which the discharge of complexed Cu$^{2+}$ occurs, and the resulting citrate is adsorbed on the surface. It was also found that the reduction of Ni$^{2+}$ ions occurred at much more negative potentials. Addition of NiSO$_4$ to CuSO$_4$ also depolarized the Cu$^{2+}$ reaction (shifted the Cu reaction to more noble potentials).

In 1988, Ying et al.\textsuperscript{21} proposed a mathematical model for the electrodeposition of Ni-Cu alloys from a citrate electrolyte when the citrate composition was greater than the sum of the metal ion concentrations. In this case the NiCit$^-$ and CuCit$^-$ are the only species involved in deposition. The following reactions were assumed to occur

\begin{equation}
CuCit^- + 2e^- \leftrightarrow Cu + Cit^{3-}
\end{equation}

\begin{equation}
NiCit^- + 2e^- \leftrightarrow Ni + Cit^{3-}
\end{equation}

\begin{equation}
2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-
\end{equation}

The following homogeneous equilibria were also included in the model

\begin{equation}
Cu^{2+} + Cit^{3-} \leftrightarrow CuCit^-
\end{equation}

\begin{equation}
Ni^{2+} + Cit^{3-} \leftrightarrow NiCit^-
\end{equation}

\begin{equation}
H_2O \leftrightarrow OH^- + H^+
\end{equation}

\begin{equation}
HCit^{2-} + H^+ \leftrightarrow H_2Cit^-
\end{equation}

Here Cit$^{3-}$ is C$_6$H$_5$O$_7^{3-}$.

The reduction of hydrogen ions from the dissociation of hydrogenated citrate ions and the reduction of dissolved oxygen were neglected. The model provided a
means of estimating mass transfer and kinetic parameters with multiple reactions occurring simultaneously.

Podlaha et al.\textsuperscript{22} in 1994, included the uncomplexed reaction rates listed below,

\begin{equation}
Cu^{+2} + 2e^- \leftrightarrow Cu \quad (2.8)
\end{equation}

\begin{equation}
Ni^{+2} + 2e^- \leftrightarrow Ni \quad (2.9)
\end{equation}

in order to simulate the case when the amount of citrate was less than the total metal ion concentrations. Differences in the kinetic rate constants were determined for the uncomplexed and complexed species. Since the uncomplexed metal ions had a more facile reaction rate, the partial current densities of both nickel and copper appeared to be inhibited in the presence of the complexant.

In addition to citrate electrolytes, sulfamate electrolytes have been used to deposit Ni-Cu alloys. Pulse and pulse-reverse plating have been used by several researchers to produce nickel-copper alloys from sulfamate solutions. Alternating layers of nickel rich alloy and copper called multilayers can be produced by varying the applied potential or current between values corresponding to pure copper deposition and a value corresponding to a nickel rich alloy. Sulfamate electrolytes of nickel and copper have been used to produce such multilayers. In 1990, Tench et al.\textsuperscript{30} studied the factors affecting the quality of multilayers electrodeposited from a single sulfamate electrolyte. They found that Ni passivation does not occur under the conditions used. They also propose the use of a low Cu concentration in the bath. Ni-Cu multilayered structures were shown to exhibit a two-fold increase in tensile strength compared to Ni-Cu obtained by dc plating from the same bath.
In 1994, Roy et al.\textsuperscript{23} proposed two models for the electrodeposition of Ni-Cu alloys from citrate electrolytes by pulsing, the corrosion model (CM) and the non-corrosion model (NCM). They showed that for short pulse off-times, the composition of alloy deposits corresponds well to that predicted by the corrosion model, and at long off-times the non-corrosion models was applicable. By comparing measured alloy compositions in pulse plating with the prediction of the CM and the NCM, one can get information about the occurrence or not of displacement reactions.

In 1996, Bradley et al.\textsuperscript{16} studied the pulse plating of copper nickel alloys from a sulfamate solution. The displacement reaction between copper and nickel occurs in a similar way as in a citrate solution. Results presented were found to confirm that the CM does predict the deposition behavior well at short pulse off-times, but with increasing pulse off-times the Cu content of the alloy approaches that of the NCM. They also found that nickel passivation does not occur under conditions used for the deposition of Ni-Cu multilayers, but a displacement of Ni by Cu during pulse off-time. This displacement reaction is mass-transport controlled. Using both sweep and linear voltammetry, they found no active dissolution of nickel in any anodic range. This seemed to agree with Menezes et al.\textsuperscript{32} who in 1990 found that displacement does not occur between Ni and Cu in a sulfamate solution. It also agreed with the findings of Tench et al.\textsuperscript{30} But as the current density approaches that of the reversible potential of Ni, the alloy is more Cu rich and inhibits the dissolution of Ni. But in pulsing Ni can dissolve. They suggest the citrate bath to be more suitable for thick Ni-Cu multilayers than sulfamate.
In 1994, L. Bonou et al.\textsuperscript{31} studied the electrodeposition and corrosion behavior of nickel copper alloys by voltammetry and impedance. The best corrosion resistance was found for a fine-grained alloy containing 60\% copper and 40 \% nickel. The corrosion resistance of this alloy was determined to be better than that of mild steel.

Yang et al.\textsuperscript{24} in 1995 investigated both the galvanostatic and potentiostatic deposition of compositionally modulated Cu-Ni alloys from a Watts bath, containing nickel sulfate, nickel chloride and copper sulfate. Theoretical models were also postulated for both methods of pulse plating. The model accounted for diffusion and kinetic control of the Ni and Cu ions. No complexing equilibria were considered. The nickel layer containing copper was assumed not to dissolve during the low current pulse. The model was the first to include the transient behavior of the diffusion controlled species in Ni-Cu alloy electrodeposition. The results indicate that the duty cycle of pulsed plating affects the current efficiency, small duty cycles of 0.2 increased the Cu content in the Ni layer. Bath efficiency drops rapidly for applied currents between 50mA/cm\textsuperscript{2} and above 200 mA/cm\textsuperscript{2}. The Cu in the Ni layer was greater than dc plating. In their second paper\textsuperscript{25} on potentiostatic deposition, results similar to galvanostatic deposition were obtained. In addition, they observed that sharper boundaries between layers occurred in the potentiostatic rather than the galvanostatic pulsing. Both experimental plating methods agreed well with their model.

In 1997, Bonhote et al.\textsuperscript{33} reported the electrodeposition of nickel-copper multilayered alloys of 20 and 10 nm, respectively from a citrate electrolyte and showed that the microstructure could be controlled. When the value of the current
density used for copper deposition was well below its limiting current density, the multilayer structure was columnar and oriented along the [110] direction. Close to the copper current density, the multilayer consisted of equiaxed grains with no preferred orientation. The citrate was shown to act as a leveling agent in the alloy deposition.

In 1998, Green et al.\textsuperscript{34} investigated the stability of the citrate electrolyte for the deposition of Ni-Cu alloys and found that pH plays an important role in the stability. The electrolyte contained 0.025-0.04 M CuSO\textsubscript{4}, 0.7 M NiSO\textsubscript{4} and 0.26 M sodium citrate. In their studies a solution of pH 4.1 is unstable as compared to a solution of pH 6.0. The same Ni content was obtained at a lower current for the pH 6.0 solution as compared to the pH 4.0 solution although the current efficiencies were similar.

Jingxian et al.\textsuperscript{35} in 1999, published experimental results on the effect of increasing amounts of copper in sulfuric acid based nickel plating solutions. The reduction potential shifted to more positive values but did not affect the mechanism of electrocrystallization. The nucleation activation energy of nickel electrodeposition decreased with increasing copper concentration in the solution.

The pH of most nickel-copper baths reported so far have involved an acidic pH. The influence of a higher pH and complexing agents such as ammonium hydroxide has also been studied. In 2000, Aravinda et al.\textsuperscript{36} studied the deposition of copper from two different alkaline complexes containing citrate – hydroxide and triethanolamine (TEA). They postulated that the deposition from the hydroxide electrolyte involves adsorption of monovalent copper species following a Langmuir isotherm and a copper species following a Temkin isotherm in the TEA electrolyte, with the adsorbed species undergoing stepwise reduction.
In 2001 Lin et al. studied the properties and microstructure of electroplated nickel from a sulfamate electrolyte containing ammonium ions. The addition of ammonium ions to the electrolyte changed the structure from a strong [100] texture to a weak [100] and a weak [110]. Ammonium ions favored the inhibited growth modes, and significantly refined the grain structure and increased the defect density. The presence of ammonium increased the internal stress and also increased the hardness of the deposit.

The influence of ammonia on the deposition of copper and nickel was also studied in 1986 by Chassaing et al., where they investigated the deposition of copper in citrate and citrate ammonia electrolytes using impedance spectroscopy. It was concluded that the addition of citrate strongly inhibits the copper reduction. The inhibition was attributed to the adsorption of free complexing species that was formed as a result of a two-step kinetic mechanism. Their model also accounted for the low current efficiency observed in the ammonia electrolytes. In 1987 the same authors extended their previous study to the copper-nickel alloy system, using both polarization and impedance techniques. They concluded that the two step discharge mechanism for copper was diffusion controlled during alloy deposition. They also proposed a two step discharge of the nickel species involving an adsorbed intermediate of nickel. These adsorbed species serve as nucleation sites for the nickel deposition.

In 1998, Natter et al. synthesized and characterized nickel and nickel – copper alloys by pulsing from an electrolyte containing tartrate and ammonium chloride. They determined that for a given deposition current the grain size of the nickel deposits decreased with increasing off-time. They also studied the effect of inhibitors on the
Ramos et al.\textsuperscript{41} in 2001 studied the influence of chloride and nitrate anions on copper electrodeposition in ammonia media. They too showed a two step reduction for the copper deposition, where the first step of Cu(II) to Cu(I) is under diffusion control and second reaction Cu(I) to Cu is influenced by the reduction of Cl\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−}. This reduction influences dissolution of copper nuclei, leading to lower current efficiencies.

In 2002, Graham et al.\textsuperscript{42} studied the nucleation and growth mechanisms for electrodeposited copper from an ammonia based electrolyte on planar substrates and in trenches on patterned silicon wafers. They found a dependence of the nucleation on the type of substrate used. With a PVD copper substrate, the growth was columnar and conformal at lower potentials. On a PVD TiN substrate, a potential-dependant incubation period was observed, where no nucleation and growth occurred. On a patterned electrode, there was preferred nucleation and growth inside the trenches. They concluded that the lower diffusivity of copper within a trench promoted nucleation and growth.

2.4 Composite Electrodeposition

Composite plating involves the reduction of metal ions from an electrolyte having suspended and undissolved powders like oxides (SiO\textsubscript{2}\textsuperscript{79}, TiO\textsubscript{2}\textsuperscript{44}, and Al\textsubscript{2}O\textsubscript{3}\textsuperscript{86}), carbides (SiC\textsuperscript{67}), nitrides (Si\textsubscript{3}N\textsubscript{4}\textsuperscript{78}), polymers (PTFE\textsuperscript{78}) and even metals (Cr\textsuperscript{85}). This results in the embedding of small solid particles into the growing metal or alloy matrix. The resultant deposits have unique properties, depending on the type of
particle incorporated, which can enhance the properties of the original metal or alloys. For example, the inclusion of alumina particles improves the hardness and wear resistance of elemental, electrodeposited Cu and Ni as demonstrated by Cu-Al$_2$O$_3$\textsuperscript{43-48} and Ni-Al$_2$O$_3$\textsuperscript{48-53} systems. The ultimate tensile strength and the yield strength are increased by almost two times as compared to metallic nickel, depending on the amount of particle incorporation.\textsuperscript{48,49} The wear resistance was found to increase with increasing alumina concentration.\textsuperscript{52} The ductility of nickel-alumina composites is however lower than nickel. Annealing of composites at high temperatures makes it more ductile but also reduces its strength.\textsuperscript{45}

In 1989, Greco\textsuperscript{61,62} published two reviews on the formation of electrocomposites and their properties. A variety of particles such as chromic oxide, chromium carbide, alumina, graphite, diamond, silicon carbide and titania with either copper or nickel was reviewed. The hardening mechanisms – dispersion strengthening, particle-reinforcement and fiber-reinforcement of various kinds and sizes of particles in a metal matrix was reported. They also reported increased hardness and strength of the electrocomposites but lower ductility and increased brittleness with increased particle concentration. Improved corrosion resistance of nickel with alumina was also reported. The reviewed literature consisted of particle dispersed composites and both discontinuous and continuous fiber-reinforced composites. In 1991 and later in 1995, Verelst \textit{et al.}\textsuperscript{51,63} also reported increased hardness and strength and lower elongation properties of nickel –alumina composites. They reported lower fragility in the case of sub-micronic particle and attributed the effect of hardening to grain growth inhibition according to the Hall-Petch law.
Hovestad et al.\textsuperscript{59} in 1994, compiled a review of electrochemical codeposition of inert particles with metals and reported the effect of parameters such as particle concentration, type, size, shape, bath constituents, temperature, pH, additives and existing models of deposition.

Several researchers have attempted to develop models to describe and predict the codeposition of particles. Theoretical models have focused on the mechanisms of deposition and predicting the amount of particle incorporation. None predict a change in the metal reaction rate due to the presence of the particle. In 1991, Celis et al.\textsuperscript{83} published a study with a review of literature on the mechanism of composite electroplating and their mathematical models.

One of the first to mathematically describe particle deposition was Guglelmi,\textsuperscript{54} who in 1972 came up with a model to describe the codeposition process. Electrophoretic attraction is the driving force behind the entrapment of particulates in the growing film. He proposed a mechanism of two adsorption steps, a) a loose adsorption, which is physical in nature and b) A strong adsorption step that takes into account the electrochemical nature of the process. The physical adsorption step (a) was described by a Langmuir isotherm similar to the approach of adsorption ions. Accordingly, the surface coverage of the particles is a function of their concentration in solution. The strong adsorption step (b) is similar to a Tafel kinetic expression and also includes a term for the loose adsorption. In this step the particles are irreversibly adsorbed. Faraday's law and a kinetic expression for the current described the volume fraction of the deposited metal. The model predicts an increase in particle concentration in the deposit with increase in the concentration in the electrolyte and a
decrease with increasing current density. They verified the process with the deposition of TiO$_2$ and SiC from a Ni-sulfamate electrolyte. It should be noted that these predictions were for the deposition on electrodes where sufficient mixing is provided and therefore mass transport and convective flows are not accounted for.

In 1974 Kariapper et al.$^{55}$ performed adsorption studies on composite coatings. They proposed that if the particles in suspension acquire a positive surface charge, they could be incorporated into the metal film by electrostatic attraction. They demonstrated the deposition of silicon carbide, titania and alumina, of a few microns in size, along with nickel from sulfamate and sulfate electrolytes.

In 1976, Lakshminarayanan et al.$^{45}$ studied the physical and mechanical properties of electrodeposited copper and copper-alumina composites. They found that the inclusion of alumina increased the yield strength, electrical resistivity and ultimate tensile strength, and reduced the ductility of the deposit. Ultrasonic agitation was helpful in improving the particle distribution and reducing agglomeration, but the deposits thus produced were more brittle. In 1977, Ramasamy et al.$^{46}$ also codeposited copper and alumina. They reported the effect of heat treatment to the composite. Stress relieving heat treatment at 500°C resulted in a drop in tensile strength and microhardness.

The Guglelmi model cannot be applied to deposition onto rotating cylinder electrodes as reported by Masuko et al.$^{56}$ in 1977, if mass transport effects are dominant. J. R. Roos et al.$^{57}$ reported the codeposition of sub micron hexagonal-$\alpha$ and spinel cubic-$\gamma$ alumina particles with copper from a sulfate electrolyte. They found a lower incorporation of $\gamma$ over $\alpha$ alumina. Celis et al.$^{58}$ in the same year also verified the
validity of the model for the deposition of alumina and copper from a copper sulfate electrolyte. They investigated the effect of monovalent cations like thallium on the volume of embedded alumina. They found that the thallium ions are not reduced themselves but act as catalysts for the reduction of adsorbed ions on the alumina and therefore increase the rate of alumina incorporation.

In 1982, Roos et al.\textsuperscript{12} demonstrated the deposition of Cu-\(\alpha\) alumina and Cu-SiC from citrate electrolytes. The alumina particles were on the order of a few microns. They studied the influence of thallium ions on the deposition of alumina and determined that they acted as a catalyst in the codeposition of alumina, consistent with their previous study.\textsuperscript{58} They also successfully codeposited gold and alumina from a gold cyanide solution on rotating electrodes.

Celis et al.\textsuperscript{59} in 1987 proposed an improvement over the Guglelmi model based on a statistical approach. They postulated a five-step adsorption process. a) An adsorbed double layer of cations forms around each particle in the bulk of the solution. b) The particles are transferred by bulk convection to the boundary layer. c) The particles diffuse through the boundary layer to reach the surface of the cathode. d) At the cathode, the adsorbed electroactive cations are reduced. e) When a fraction of the ions originally adsorbed on a particle are reduced, the particle is captured by the growing film. The model predicts the volume fraction of codeposited particles from the probability of a particle crossing the diffusion layer to become incorporated, the number of particles arriving at the cathode and the weight of the particle. The probability of a particle being deposited at a given current is based on a binomial distribution and incorporates the bulk concentration and diffusion coefficient of the
metal and the boundary layer thickness. The validity of the model was verified for the codeposition of alumina with copper from an acid copper sulfate bath.

In 1987 Valdes et al. attempted to theoretically explain the mechanics of the codeposition by accounting for the electrochemical and hydrodynamic forces acting on particles. They introduced the concept of a “perfect sink” method that corresponds to infinitely fast kinetics. All particles approaching within a certain critical distance are captured. The particle flux has a convective term and a diffusion term. The convective velocity takes into account the contributions from hydrodynamic convection, electromigration and diffusiomigration and other specific forces of attraction. The perfect sink model predicts the rate of particle deposition increases with increasing current density and attains its maximum value, which plateaus at the limiting current density. This phenomenon was observed only for particle deposition from a binary electrolyte, where the effect of the electric field generated is more pronounced and the effect of diffusiomigration and electromigration on particle transport is appreciable. In a system with an excess of supporting electrolyte, the field generated is not sufficient to provide any significant transport of colloidal particles by electromigration. An Electron-Ion Particle Electron Transfer (EIPET) kinetic model was developed, where an additional parameter, defined as an electrochemical Damkohler number was introduced to relax the perfect sink assumption and characterize the interfacial deposition step. Electroactive ions adsorbed on the particles are reduced and the main driving force of particle deposition is the charge transfer overpotential. The model predicts that the rate of codeposition increases with increasing current density until a maximum and then decreases. The decrease in particle deposition rates occurs because
the deposition is in the limiting current region and for smaller values of the Damkohler number, the kinetics of metal deposition becomes the rate determining step, despite increased rates of particle transport. The results obtained were in concordance with the experimental data of the deposition of alumina particles from an acidic copper sulfate electrolyte.

In 1988, Chang et al.\textsuperscript{52} reported improved wear resistance with submicron alumina particles codeposited from a Watts bath onto stationary electrodes. The concentration of alumina particles in the bath was less than 1.5 g/l. The composition of alumina in the deposit was higher at lower current densities and was as high as 20%.

In 1992, Fransaer et al.\textsuperscript{64} introduced a trajectory model, which is appropriate for large particle size > 1 micron, unlike that of Valdez, which included Brownian diffusion and is most appropriate for submicron size particles. The forces acting on large particles were accounted for as: a) forces on the particle due to the convection of the fluid and b) body forces on the fluid such as gravitation and buoyancy. The trajectory of a particle can be determined from the equation of motion. The limiting particle trajectory is defined as the trajectory, of the approaching particle, which will make contact with the electrode. The model was tested on a RDE for the deposition of polystyrene particles with copper. It predicts that the concentration of particles decreases with radial position and decreases more rapidly as the rotation rate increases. As the rotation rate increases, the shearing force increases and particles leave the surface of the electrode depending on the relative magnitude of the shearing force and the adhesion force.
In 1993, Hayashi et al. determined that the adsorbed ions from the plating bath are essential in particle incorporation of alumina with copper from an acid sulfate electrolyte. Despite the negative value of the zeta potential, incorporation of alumina with copper could be achieved. This indicated that the adsorption of copper ions on the particle and not the electrostatic interaction between particle and electrode plays an important role in the codeposition. The surface adsorption and corresponding reduction at the cathode were found to be the important step in the codeposition of silicon carbide with nickel as reported by Hwang et al. in 1993 and with cobalt as reported by Yeh et al. in 1994.

Webb et al. in 1994, found that the nickel polarization behavior and current efficiency of deposition was substantially altered by the presence of alumina particles. The nickel current was shifted to more negative potentials in the presence of alumina. This anomalous behavior was attributed to a partial blocking of the portion of the electrode surface by the particle and competition between the charge transfer nickel reaction and mass transport limited alumina. No prior models had included the influence of the particle on the metal rate.

In 1995, Fransaer et al. proposed a theoretical model to describe the variations in the flow of current to disk electrodes caused by a finite number of spherical and prolate particles. They developed a boundary collocation method to calculate the resistance variations and the influence on current in the presence of particles and in their absence. The increase in resistance to the flow of particles was determined as a function of the diameter of the particle. Larger particles increase the resistance to a greater degree than smaller ones. The primary current distribution
around a particle was plotted as a function of the aspect ratio of the particle. The position of the particle was also determined, from its influence on the current as it flows past the electrode.

Fawzy et al. \(^{44}\) in 1995 reported the codeposition of alumina and titania with copper from acid electrolytes with increased microhardness. Maurin et al. \(^{84}\) in 1995, studied the codeposition of silicon carbide particles with nickel from a Watts bath on a rotating disc electrode. They found that the particle incorporation is governed not only by adsorption but also on the fluid velocity. The normal component of the velocity promotes particle impingement, whereas the tangential component tends to eject them. The relative magnitudes of these forces determines the incorporation into the metal matrix. In 1997, H. Ferkel et al. \(^{53}\) also produced dispersion hardened nickel and nanometric alumina films from a Watts bath.

In 1997, Podlaha et al. \(^{71}\) developed a pulse reverse plating scheme to enhance the concentration of nanometric \(\gamma\)-alumina in a copper matrix from an acidic pH citrate electrolyte. Particles were incorporated during the metal ion reduction during the cathodic pulse. A part of the metal was dissolved during the anodic pulse resulting in an enhancement of the alumina concentration. Vidrine et al. \(^{72}\) in 2001 have also investigated the pulse reverse scheme to deposit \(\gamma\)-alumina, with an average diameter of 32 nm in a nickel matrix from citrate and chloride electrolytes. A pulse reverse scheme could not be carried out for the citrate electrolyte due to the formation of a passivating region between -0.2 and -1.2 V vs. SCE. The chloride electrolyte does not show a passivation region. They found that the particle concentration in the deposit decreased with current density in the chloride bath but increased for the citrate bath.
The current efficiency improved with increasing applied current density for both baths. Thus the citrate electrolyte was found to be the most attractive for further optimization. Podlaha\textsuperscript{81} again in 2001 demonstrated the selective electrodeposition of nanoparticles of alumina into a copper matrix from a citrate electrolyte using a pulse – reverse method. The pulse reverse scheme helped produce nanocomposites with particle size distribution control, where the incorporated particles were below 30nm in size and larger particles were absent. There was also an enhancement of particle deposit concentration under conditions of pulse reverse plating.

Ding \textit{et al}.\textsuperscript{48} in 1998 used submicron particle sizes of alpha-alumina (0.11 micron and 0.4 micron) and showed that there is a linear increase in microhardness in both Ni and Cu with particle volume fraction in the deposit. The smaller particles produced a larger hardening effect and the strengthening mechanism was explained by a combination of the Orowan-type strengthening and Hall-Petch effects.

Stojak \textit{et al}.\textsuperscript{73,74} in 1999 and 2000 have investigated the influence of alumina on the electrocodeposition of Cu from an acidic copper sulfate bath. The effects of particle loading, size and crystallographic phases, hydrodynamics and electrode orientation were studied. The incorporation of $\gamma$-alumina was found to be at least three times greater than $\alpha$ alumina. The particle incorporation increased as a function of applied current density for all rotation rates. They assumed the rate-determining step to be the reduction of metallic ions adsorbed onto the alumina particles. It reaches a maximum and then decreases, as the rate of metal deposition increases, to a region where the composition is relatively constant. The peak of particle incorporation as a function of the current coincides with the point of zero charge (pzc) of Cu in an acidic plating
solution. The solution conductivity decreases with increasing particle loading. The current in the kinetic and mixed control regions in solutions with particles is lower than in solutions without particles. The mass transport is not decreased. For large particle loadings (> 158 g/l) an enhancement of the mass transport was observed.

Wang et al.\textsuperscript{75} in 1999 developed an adsorption strength model to describe the mechanism of codeposition of $\alpha$-alumina and a Fe-P alloy. The postulates of the model were a) Particles adsorbed on the cathode surface can detach again. A dynamic equilibrium is set up during deposition. b) The intensity with which a particle sticks to the cathode surface is described in terms of the adsorption strength, which conforms to a normal distribution. c) A particle may be incorporated into the deposit, when its adsorption strength is above a critical value. The probability of particles being effectively adsorbed is a function of the adsorption strength between the particle and the cathode. The weight of the embedded particles is expressed as a function of the surface coverage of particles, the probability, radius of the particle and the applied current density. The average adsorption strength increases and the coverage decreases with increasing current density. The model predicts a maximum in the particle concentration with increasing current density.

In 2000, Vereecken \textit{et al.}\textsuperscript{76} described the kinetics of nanometer sized particles into a growing film by taking into account the convective diffusion of particles to the surface and treats the incorporation in terms of the residence time. A nickel and $\gamma$-alumina composite was grown from a sulfamate electrolyte. The rate of codeposition depends on the rate of metal deposition and the flux of particles to the film surface. When the growth of the film is fast in comparison to the residence time of the particle,
all particles are trapped at the surface and the particle concentration at the surface is zero. The volume fraction of \( \text{Al}_2\text{O}_3 \) increases with increasing rotation rate and decreases with increasing current density. This is similar to an ionic mass transfer process. The model holds for particles with a diameter less than 1 µm and when the diffusion layer thickness is larger than the particle size.

In 2000 Musiani\(^77\) and Kerr \textit{et al.}\(^78\) reviewed numerous methods of electrodeposition of composites and their applications. Nowak \textit{et al.}\(^79\) in 2000, utilized impedance spectroscopy to study the codeposition of SiC and SiO\(_2\) with nickel. SiC codeposits readily while SiO\(_2\) does not. Silica was found to increase the electrode capacitance, and increase surface roughness, but SiC decreased the capacitance and was readily adsorbed on the surface leading to surface blockage. They suggest that the particles are adsorbed but not embedded in the electrode and remain separated by a liquid film. The rupture of this liquid film was assumed to be the key controlling factor SiO\(_2\) incorporation. SiO\(_2\) is hydrophilic and hence does not approach the surface as readily as silicon carbide and does not incorporate as readily.

In 2001 Fransaer \textit{et al.}\(^80\) have postulated that the hydrophobic and hydrophilic nature of particles play an important role in the extent to which they are incorporated in the deposit. The variation of the adhesion force with current density was identified as being linked to changes in the hydration force. The hydration force results from a change in the structure of water under the influence of a substrate force field. They explained the dependence of particle codeposition on the type of particles used in terms of the hydrolizable nature of the oxide, carbide or polymer. Most oxides are hydrophilic in nature and as a result the hydration force acts as a force of repulsion.
between the cathode and the particle. Oxides, such as alumina and silica, which carry a large amount of adsorbed metallic ions on their surface, block the surface of the cathode and lead to a local rise in pH, which creates conditions favoring the co-deposition of particles. These ions adsorbed on the surface significantly govern, but are not the determining factor, for incorporation.

J. Steinbach et al.\textsuperscript{50} in 2001, produced nickel alumina composites with both direct and pulsed current schemes, from a sulfamate electrolyte. The average particle size was 25 nm. Under conditions of pulsed current the included particle sizes were smaller than those under conditions of direct current.

### 2.3 Electrodeposition in Recessed Geometries

Several research efforts have been directed towards describing the process of deposition in lithographically patterned electrodes and into recesses. The dimensions of these recesses usually range from sub-micronic to a few hundred microns deep. In 1988, Bond et al.\textsuperscript{88} compared the chronoamperometric response of dimensionally identical recessed and planar microelectrodes (RDE). During chronoamperometry, a recessed disc electrode displays cottrellian behavior initially and then with time approaches a steady state. Expressions describing, both short and long-term behaviors of the transient process of a single, elemental mass transport controlled deposition were presented and found to fit well with experimental results. In 1991, West et al.\textsuperscript{89} modeled the primary current distribution and ohmic resistance for various aspect ratios, in the absence of concentration variations on a recessed electrode. They presented mathematical expressions for the ohmic resistance and the radial current distributions from the center to the edge of the electrode. Dinan et al.\textsuperscript{20} in the same
year also conducted experimental investigations of the primary current distribution onto recessed rotating disk electrodes. They found that the ohmic resistance of the recessed-disk electrode was found to increase linearly with aspect ratio and the mass transport rate decreased with increasing aspect ratio. For aspect ratios greater than 0.5, the deviation of the current density at the edge of the electrode from the average current density was less than 10%.

Leyendecker et al.\textsuperscript{90} in 1994 and Bade et al.\textsuperscript{91} in 1995 studied the mechanism underlying the deposition of Ni in microholes using a rotating microstructure electrode (RME). Mass transfer was the limiting factor. A 1-D diffusion model was used to describe the process, and the diffusion layer was equal to or less than the photoresist thickness depending on the aspect ratios of the recess. M. Kupper et al.\textsuperscript{92} measured the local concentration distributions within microstructures, alloy composition along all three axes, the effects of side reactions and the influence of convection on the electrodeposition in microstructures with a Cu-Ni system using a phthalate electrolyte. They found that with aspect ratios greater than 1.5 the effects of side reactions on the metal deposition increase and the formation of nickel oxide and hydroxide was possible. This in turn blocked the deposition of Ni due to inhibition of the cathode. The concentration distribution was also found to be uniform for higher aspect ratios.

In 1998, Griffiths et al.\textsuperscript{93} developed both one and two-dimensional models describing the electrodeposition of metals into high-aspect ratio molds. The one-dimensional model addresses diffusion, electromigration and deposition of multiple ion species (Ni-Fe). The two dimensional model is limited to a single species (Ni), but includes transport induced by the forced flow of electrolyte outside the recess and
buoyancy associated with metal ion depletion within the recess. They studied the effect of surface pH on the morphology of deposits. High pH’s at the deposition surface leads to poor metal morphology and hydrogen generation, and high surface pH’s were evident even when applied current densities were only about 20% of the theoretical limiting current value. At high current densities nodular deposits were observed. They have postulated that buoyancy driven convection is responsible for enhanced mass transport and can increase plating rates. Andricacos et al.\textsuperscript{94} in 1998 developed a model for the deposition of copper for chip interconnections based on inhibition by diffusion-controlled additives. Shape-induced concentration-fields result in a wide range of fluxes in the profile of the recess. They have called their superconformal deposition process superfilling. It was found to agree well with experiments as reported in a later paper by Andricacos\textsuperscript{95} in 1999.

In 1999, West et al.\textsuperscript{96} developed a theoretical model based on a one-dimensional approximation, for the filling of high aspect ratio trenches and vias with copper by pulsing and pulse reverse plating. They concluded that to minimize void size, the off-time of a pulse cycle should be on the order of the diffusion time constant and the deposition time should be smaller than the diffusion time constant. Reverse currents improved the distribution of the time averaged deposition rates along the sidewalls of the trench. Again in 2000, West\textsuperscript{97} employed numerical simulations to estimate the importance of leveling agents on the electrodeposition of Cu in trenches and vias. Void formation was predicted if the concentration of additives was too high or too low, and as feature sizes were reduced, the depositions tend to become conformal.
In 2001 Gill et al. developed a model to predict the effect of a buffering agent in the plating bath. They have formulated a mass transfer pulse-plating model for a copper complex where, the rate of dissociation of the complex is proportional to the driving force applied. They found that the presence of a buffering solution, using small duty cycles and pulse periods increases the conformality of the deposit and ensures better gap filling.

In 2001, Namburi demonstrated the electrodeposition of Ni-W alloys into 500 \( \mu m \) deep recesses made by x-ray lithography. A pulse scheme similar to that reported in this dissertation was used to overcome the effects of the side reactions and diffusional constraints of the depositing species.

### 2.4. Composite Deposition in Recesses

Even though the deposition of composite coatings on flat and cylindrical geometries has been achieved, very little work exists on their deposition into recessed geometries. Wang in 1999 has demonstrated the deposition of \( \gamma \)-alumina and nickel from a nickel sulfamate electrolyte with varying alumina concentrations at acidic pHs. Two different electrode setups - a horizontal one and a vertical one were investigated. In the vertical setup, two distinct regions divided by a slanted boundary were evident – one with high and the other with lower alumina concentrations. The region at the bottom of the recess had lower alumina concentration than at the top and can be attributed to the weaker agitation deep inside the recess. In a horizontal setup, the distribution was more uniform. The resulting microposts had an average alumina concentration of about 40-wt \% alumina. This high percentage was due to the extremely agglomerated particles in the electrodeposit.
In 1999, Yeh et al.\textsuperscript{101} demonstrated the DC electrodeposition of micron and submicron sized SiC and Ni from a nickel sulfamate bath of a hundred microns thick film for MEMS applications. It was found that the particulate concentration in the deposit increased with increase in the powder concentration in the electrolyte, so did the internal stress. Lower currents decrease the internal stress in the deposit. Hardness was found to improve and a smoother surface was obtained with finer particles.

In 2000, Flores et al.\textsuperscript{102} have deposited Cu and $\gamma$-alumina by potentiostatic deposition from a citrate electrolyte at a pH of 4.0 into recesses 500 micron deep. The resulting microstructures contained 3\% by weight of alumina on an average, but poor adhesion and void formation was evidenced.

Jakob et al.\textsuperscript{103} in 2000, deposited nanometric alumina and titania along with nickel from a Watts bath in microstructures for tribological applications. The depths of the recesses were about 50 $\mu$m. They reported a high concentration of alumina in the electrolyte (5 volume\%). They observed agglomeration of the particles and a height dependent incorporation. No explanation was provided for the diffusion control, incorporation rate or the incorporation distribution.

2.5 LIGA Microdevices

Among the first microdevices demonstrated, were the electrodeposition of lithographically patterned features introduced in the early 1960’s by IBM to increase memory density and reduce the physical size of memory devices. To ensure lower current densities in the conductors and to avoid electromigration, it became necessary to make the conductors thicker.\textsuperscript{1} In achieving this aim conventional deposition methods of thicker films, followed by lithography and chemical etching, encountered
limitations. It was not possible to place conductors or devices more closely than twice
the thickness of the films in which they were etched. Romankiw et al.\textsuperscript{1} have concluded
that the best method of achieving the highest pattern density is by using a thin seed
layer, applying a thick polymeric resist, patterning the resist with an inverse pattern,
electrodepositing the metal into the recesses and subsequently removing the resist and
the thin seed layer to create a 3D pattern. This has evolved today into what is known
as through-lithographic mask technology.

Romankiw et al.\textsuperscript{105-107} at IBM’s Thomas J. Watson Research Center were the
first to carry out the electroplating of copper conductors through lithographic resist
masks in 1965. This was done to create copper wires on thin seed layers used to form
an experimental version of a coupled magnetic memory. Later, the same process was
utilized by Andricacos et al.\textsuperscript{108} in 1994 and Romankiw et al.\textsuperscript{109} in 1990 to
electrodeposit both thin and thick film magnetic heads made of permalloy for data
storage. In 1982 the process was once again demonstrated by Becker et al.\textsuperscript{110} in
electrodepositing nickel into a pre-patterned high-aspect-ratio recess at KfK in
Germany for the fabrication of uranium separation micronozzle. This is widely
considered to be the first demonstration of a LIGA microdevice.

Since then, LIGA microstructures have found a variety of applications in X-ray
masks, sensors and actuators, microoptics, microelectronic devices and
micromechanical systems. Numerous metal, alloy and polymeric microstructures and
microdevices have been produced and investigated for a variety of MEMS
applications. For example, Maner et al.\textsuperscript{111} in 1989 made electronic microconnectors,
Krongelb et al.\textsuperscript{112} in 1995, have recently enhanced the process using an integrated
combination of electrochemical and wet and dry technologies and have fabricated stacks with multiple layers of conductors using through mask electroplating. These are used as cost-effective interconnections for a variety of microelectronic devices and machines. In 1989, Benecke and Rietmuller \cite{benecke1989} presented a microactuator based on a bimaterial effect, used extensively in the fabrication of temperature controlled electrical switches. In 1991, Bley et al.\cite{bley1991} have fabricated a microgear made of nickel. Leith et al.\cite{leith1999} in 1999 have also demonstrated a microgear of nickel iron made by the selective etching of iron rich layers, which were made by modulating the composition by using pulsed electrolyte agitation. Wallrabe et al.\cite{wallrabe1992}, in 1992 designed, fabricated and successfully tested an electrostatic stepping micromotor using the electrostatic principle. Electromagnetic activation has been used by Mohr et al.\cite{mohr1992} in 1992 to measure the fatigue behavior of micromechanical elements made of electroplated nickel.

In 1993, Schomburg et al.\cite{schomburg1993} demonstrated a microvalve. In 1993, Guckel et al.\cite{guckel1993} produced a micromotor based on the electromagnetic principle by using four stacked layers. In 1995 they also demonstrated magnetically driven linear actuators.\cite{guckel1995} In 1994, Lochel et al.\cite{lochel1994} demonstrated a three-dimensional micro coil winding made of nickel-iron. In 1995, a microturbine was fabricated at the Center for x-ray lithography (CXRL) in Wisconsin utilizing 500-micron thick nickel turbine and plated copper stator.\cite{schomburg1995} In 1996, Acosta et al.\cite{acosta1996} have designed, fabricated and operated a variable reluctance magnetic motor using permalloy rotors and stators. Doppler el et al.\cite{doppler1996} have also microfabricated gear pumps for viscous fluids. In 1997 Fischer et al.\cite{fischer1997} examined two methods to increase structure heights using the single layer technique and the
multi-layer stacking technique. Single layer devices have the advantage of ease of assembly, since assembly adds a step to batch fabrication along with other alignment and clamping issues and techniques. The disadvantages are long development cycles and electroplating times. Owing to the strong demand for fiber optics in high data transfer, microactuators of ferromagnetic materials like Ni and NiFe have been used by Lehr et al.\cite{Lehr124} to make fiber optic switches.

In 1997 Liu et al.\cite{Liu125} fabricated microchannels by molding glass onto a 20:1 and 150 µm high pattern made out of nickel. In 1998 Ford et al.\cite{Ford126} have demonstrated an integrated microdevice comprising of a piezo-driven micropump and a microelectrophoresis device with a fluorescence detector out of PMMA. A electromagnetic actuator by plating nickel-iron permalloy in the shape of a micromachined horseshoe type inductor was made by Sadler et al.\cite{Sadler127} in 1999. Later in 2001, they reported an eddy current sensor\cite{Sadler128} consisting of coils of nickel-iron permalloy as at he magnetic core to fabricate a proximity sensor capable of detecting cracks on the order of a few hundred microns. Bauer et al.\cite{Bauer129} used the LIGA process to produce optical waveguides used in telecommunications by compression molding of PMMA. Soper et al.\cite{Soper130} in 2001 demonstrated a microfluidic device made by the LIGA process from PMMA or PC to identify genes associated with cancer causing genes, by ligase detection reactions using either micro-electrophoresis or DNA microarrays. Katsarakis et al.\cite{Katsarakis131} in 2002 have produced a metallic photonic band-gap crystal for use as filters in high-frequency devices. They used square and triangular lattices of nickel posts 800 µm tall in PMMA. Morales et al.\cite{Morales132} have produced complex metal cantilevered microstructures on multiple levels. In 2003, Oka et al.\cite{Oka133} have developed
a micro-optical distance sensor using a combination of micromachining and the LIGA process.

2.6 Materials for LIGA

Ehrfeld et al.\textsuperscript{136} in 1999 have reviewed the current metal-based materials in use for the electrodeposition of LIGA products. A brief selection of the materials that they have outlined is summarized in Table 2.1. The properties of these alloys and composites are important while considering their applications for MEMS. Ni-P alloys have been found to have good wear intensity. Hard microstructures of Co-W and Ni-W alloys used for making mold inserts and micro injection molding. Ni-Fe is also used for fiber-optic switches and samarium-cobalt (Sm-Co) alloys are used for magnetic actuators. Metal matrix composites (MMC), which include micro or nanoparticles of Al\textsubscript{2}O\textsubscript{3}, SiC, SiO\textsubscript{2}, TiN and diamond, are considered to be promising candidates to incorporate into nickel matrices for MEMS applications. None however have been demonstrated thus far in microdevices.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Applications} & \textbf{Metals} & \textbf{Alloys} \\
\hline
Mold insert & Ni, Cu & Ni-Co \\
\hline
X-ray absorber & Au & \\
\hline
Micromechanics & Ni & Ni-Co, Ni-P \\
\hline
\end{tabular}
\caption{Electrodeposited Materials for LIGA}
\end{table}
Table 2.1 continued

<table>
<thead>
<tr>
<th>Sensors and Actuators</th>
<th>Fe</th>
<th>Ni-Fe</th>
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<td>Sacrificial layers</td>
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</tr>
<tr>
<td>Functional coatings</td>
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<td></td>
</tr>
<tr>
<td>Electrical contacts</td>
<td>Au, Cu</td>
<td></td>
</tr>
<tr>
<td>Slide bearings</td>
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<td></td>
</tr>
<tr>
<td>Others</td>
<td>Ag, Cu</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 3.

EXPERIMENTAL DESIGN

The experimental setup, substrate preparation, apparatus and electrolytes used, and methodology of characterization are described in this chapter. A typical three-electrode system is used for the electrodeposition process. Figure 3.1 shows the schematic setup of such an arrangement. The cathode, which may be movable or stationary, is the working electrode (WE) on which metal is deposited, while the anode serves as the counter electrode (CE). A reference electrode (RE) is placed as near the cathode as possible to reduce the ohmic drop effect. The current or the potential can be controlled by a galvanostat or potentiostat, respectively.

Figure 3.1 Schematic of a standard three-electrode cell.
3.1 Recessed Electrode

3.1.1 Substrate Preparation

The deep recesses were prepared on a 500-micron polymethylmethacrylate (PMMA) sheet fixed onto a copper substrate. Electrodes for deep recess plating were fabricated at the Center for Advanced Microstructures and Devices (LSU-CAMD). A square copper plate 5.0 cm x 5.0 cm with a thickness of 0.9 mm was used as a substrate. The copper plate was mechanically polished and thoroughly cleaned with soap, water, and acetone and then rinsed with a 10% sulfuric acid solution for 2-3 minutes, followed by a final rinse in deionized water. To promote adhesion to the PMMA sheet the copper surface was oxidized by placing it in a solution shown in Table 3.1 at a temperature of 95°C for 20 minutes. It was then rinsed in deionized water and dried.

Table 3.1 Composition of the oxidizing solution used to oxidize copper electrode

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO₂</td>
<td>54.26</td>
</tr>
<tr>
<td>NaOH</td>
<td>68.00</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>11.44</td>
</tr>
<tr>
<td>NaCl</td>
<td>4.67</td>
</tr>
</tbody>
</table>

3.1.2 Bonding

The 500 µm thick PMMA sheet was bonded to the copper substrate using the bonding solution provided in Table 2. The order of mixing is important: MMA and
DMA are mixed together first, followed by the addition of powdered PMMA and BPO, and stirred for 6-8 hours. A few drops of the bonding solution were dropped on the oxidized copper surface and pressure of about 10 PSI was applied immediately to the substrate and was left overnight to let the bonding solution solidify.

**Table 3.2** Composition of bonding solution used to bond PMMA and Cu/CuOx electrode

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Methacrylate (MMA)</td>
<td>0.919</td>
</tr>
<tr>
<td>Powdered PMMA</td>
<td>0.055</td>
</tr>
<tr>
<td>Benzoyl Peroxide (BPO)</td>
<td>0.0164</td>
</tr>
<tr>
<td>Dimethyl Aniline (DMA)</td>
<td>0.011</td>
</tr>
</tbody>
</table>

### 3.1.3 Lithography of PMMA

X-ray lithography is based on the principle of high energy collimated x-rays generated from a synchrotron radiation facility are incident on a 2-D mask patterned with a high atomic number absorber and a low atomic number membrane or an open area. The x-rays pass through the membrane or open area of the mask and induce exposure of PMMA. The exposed PMMA becomes soluble because of the chain scission of PMMA occurring under radiation, and can be removed with chemical solvents. The removal of the exposed PMMA is called development. The conductive or base layer in the developed region is then electroplated with desired metals or alloys to form the required deposits. The resulting metallic structure can also be used for
replicating the complementary pattern for the next stage of replication. A schematic of the exposure is shown in Figure 3.2.

The bonded PMMA/Cu sample was placed behind a tantalum (Ta) membrane mask and exposed to collimated X-rays (wavelength 4Å) at either XRLM-2 or XRLM-3 beamline at either 1.3 or 1.45 GeV at CAMD. An aluminum filter was placed in front of the Ta mask to absorb lower energy photons so that the appropriate ratio of top dose to bottom dose received by PMMA can be ensured. The bottom dose of the exposure was 3500 J/cm³ which was enough to ensure complete development. A top to bottom dose not exceeding 7.5 was used with a scan length of 0.4 inches and scan speed of 0.5 inch/s. The conditions for exposure are listed in Table 3.3. Two different Tantalum masks were used in this study. One was a pattern of circular holes, 200 µm in diameter, 1mm apart and a square pattern with 187 x 187 µm squares, 20 µm apart. The thickness of the resist in all cases was 500 microns.

3.1.4 Development and Rinsing

After exposure to x-rays, the PMMA was developed and rinsed. This is a two-step process involving removal of the PMMA, which was exposed to x-rays during lithography - by dissolving it in the appropriate solvent (developing) followed by a rinse step. The rinse process for PMMA is usually longer than the developing process. The components of the developing solution are shown in Table 3.3 consists of 60% (2-butoxyethoxy) ethanol (diethylene glycol), 20% morpholine, 5% 2-aminoethanol and 15% deionized water, all in volume percentages. The rinse solution, shown in Table 3.4 is (2-(2-butoxyethoxy) ethanol (diethylene glycol) (80%) and deionized water (20%), all in volume percentages.
Four cycles of 15 minutes each in the developer, 2 minutes in the pre-rinse and 60 minutes in the rinse were used with agitation by a magnetic stirrer in a beaker. The pre-rinse consisted of diluted older rinse solution, if not available plain deionized water was used. Development and rinsing can also be carried out with ultrasonic agitation\textsuperscript{138}.

\textbf{Figure 3.2.} Schematic of the x-ray lithography process
(Branson, Model #1510). This helps in a faster developing time, but ultrasonication also results in the production of heat. Prolonged agitation on an ultrasound resulted in delamination of the resist from the copper oxide surface and cracking was observed in the exposed regions. Therefore it is essential to allow the developer and rinse solutions to cool down between cycles. Three cycles were found to be sufficient to completely develop the sample. A pre-developer step comprising of older developer solution diluted with water was also introduced before the development step. Following the development and rinse procedure the sample was left stirring in a beaker with DI water to ensure complete removal of developed material.

**Table 3.3** Conditions of exposure of 500 µm PMMA at CAMD beamlines.

<table>
<thead>
<tr>
<th>Beamline</th>
<th>Be Filter (µm)</th>
<th>Al Filter (µm)</th>
<th>Energy (MeV)</th>
<th>Dose (mA.min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRLM-2</td>
<td>175</td>
<td>16</td>
<td>1.3</td>
<td>11300</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>16</td>
<td>1.45</td>
<td>3878</td>
</tr>
<tr>
<td>XRLM-3</td>
<td>250</td>
<td>16</td>
<td>1.3</td>
<td>3655</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>16</td>
<td>1.45</td>
<td>11808</td>
</tr>
</tbody>
</table>

**Table 3.4** Components of developing solution used to remove the exposed PMMA

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylene glycol butyl ether</td>
<td>600</td>
</tr>
</tbody>
</table>
Table 3.4 continued

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morpholine</td>
<td>200</td>
</tr>
<tr>
<td>2-aminoethanol</td>
<td>50</td>
</tr>
<tr>
<td>Water</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 3.5 Components of the rinse solution used to remove the exposed PMMA.

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylene glycol butyl ether</td>
<td>800</td>
</tr>
<tr>
<td>Water</td>
<td>200</td>
</tr>
</tbody>
</table>

3.1.5 Etching

Just before electrodeposition etching of the substrate was carried out to remove the copper oxide at the bottom of the recess in the developed areas. This exposes the conductive copper substrate below the copper oxide to the electrolyte and allows the flow of current. Table 3.4 lists the composition of the etch solution used. This was followed by rinsing it in deionized water for 4-5 minutes. It was then placed in the electrode holder for electroplating.
Table 3.6 Components of the etch solution used to remove the copper oxide.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium chloride</td>
<td>0.5</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>0.5</td>
</tr>
</tbody>
</table>

3.2 Holder Design

Figure 3.3 is a schematic of the electrode holder used in the experiments. The electrode holder consisted of two circular PEEK or acrylic discs of radius 5 cm and thickness of 0.9 cm was used. The top disc had the center cut out in the shape of a square of dimension 3 cm x 3 cm. This provides a plating area of approximately 2.5 cm² on the square patterns and 0.0872 cm² on the circular holes pattern. This section provides the only contact that the substrate has with the electrolyte. The top disc also has 2 O-rings embedded in grooves to make the substrate watertight from the sides. This ensures that the outer solution is not able to reach the electrode from the outer sides and does not seep in from the inner square. The outer O-Ring was circular and at a distance of 4 centimeters from the center. Eight equidistant holes of 5.1 mm diameter were drilled between the O-Ring and the outer edge of the disc. Identical screw holes were drilled in the bottom disc. The inner O-ring was placed in a square groove just slightly bigger than the inner square.

The bottom disc consisted of a square copper plate of 5 cm x 5 cm embedded into a recess on the plastic disc so that the entire surface was planar. A hole was drilled through the center of the disc from the backside to provide electrical contact by means
of an insulated copper wire. The hole was later sealed off with resin to insulate the bottom of the electrode from the electrolyte. The developed recessed electrode was placed with the conductive side flush with the copper plate on the bottom disc and the two discs were screwed together with plastic screws. The entire electrode holder setup was then rinsed in water and placed in the ultrasound bath prior to electrodeposition to ensure that all air bubbles inside the recesses were completely removed. The top of the substrate-PMMA electrode was recessed from the edge of the holder 1 cm to promote current distribution uniformity across the features.

Figure 3.3 Top views of (a) the top of the electrode holder and (b) the bottom of the electrode holder.
3.3 Plating Cell Setup

A schematic of the electroplating cell used, is shown in Figure 3.5. The deposition system includes a reaction kettle made of Pyrex glass of 2000 ml capacity. The entire electrode assembly is suspended by two nylon rods, 1 cm in diameter, screwed onto the electrode holder diametrically opposite to each other. A perforated nickel plate 6 x 6 cm was used as the anode, affixed to one of the rods used to support the electrode holder. It consisted of 25 holes (0.5 cm in diameter) in a square pattern. The holes were 0.5 cm in diameter and their centers were 1 cm apart. An insulated copper wire was used for electrical contact to the anode. This was affixed to one of the rods used to support the electrode holder with electrical insulating tape such that the plate was 2 cm above the surface of the holder and parallel to it. The perforations on the anode are important for the uniform agitation of the electrolyte with particulates. Vigorous agitation using both mechanical agitators (Arrow, Model No. 1750) and magnetic stirrers (Corning Inc.) was used to keep the electrolyte in a uniform suspension and to prevent sedimentation and localized concentration gradients.

A horizontal face up orientation, in contrast to a vertical orientation also helps the gas bubbles generated during plating to escape out of the recess. Additionally nanoparticles tend to settle uniformly within the recess and avoid geometry dependant distributions. The electrode was etched just before plating and allowed to stand in solution for at least five minutes before any experiments were conducted to ensure that trapped water in the recesses was allowed to diffuse out and the electrolyte could diffuse in and attain equilibrium.
Figure 3.5 Schematic of face-up recessed electrode setup.

3.4 Rotating Cylinder Electrode

Rotating Cylinder Electrodes (RCE) are often used in laboratory experimental studies of electrodeposition due to their capability of providing controlled hydrodynamic flow. Mass transport and kinetic information can then be easily decoupled. Preliminary experiments were performed on the rotating cylinder electrode before proceeding to the recessed electrodes.
Figure 3.5 shows a typical recessed rotating cylinder electrode setup. The advantage of using a recessed rotating cylinder electrode is that the primary current distribution is more uniform compared to a conventional rotating disk electrode commonly employed in electrochemical studies. The rotating cylinders used were 1.2 cm long and 1 cm in diameter and made of 410 stainless steel and plated with 0.5 µm of gold.

**Figure 3.5** Schematic of recessed rotating cylinder electrode setup.

### 3.5 Instrumentation

All impedance measurements, current/potential decay and polarization experiments were performed using a computer equipped BAS-Zahner IM6 (e) system with real time data acquisition software. The EG&G Princeton Applied Research
Potentiostat/Galvanostat (Model 363) along with the EG&G PARC Universal Programmer (Model 175) or an Amel Instruments Potentiostat (Model 2051) coupled with a Wavetek DDS function generator (Model 29) for pulsed current and dc waveforms were used to perform pulse plating and also DC plating. A saturated calomel electrode (SCE, Corning) was used as a reference electrode to measure the deposition potential relative to the working electrode. A Thermo Orion (Model# 420) pH meter with a temperature sensing probe with a KCl pH electrode (Orion 91-57) was used to measure the pH.

3.6 Electrolytes

Ni-Cu alloy electrodeposition experiments citrate electrolytes. Super pure de-ionized water of 18 mega ohms-cm was used in making up the electrolyte. The Nickel concentration was kept in great excess of copper to obtain alloys rich in nickel. Two different pHs were investigated – one at pH 4.0 (with sulfuric acid) and another at pH 8.0 (with ammonium hydroxide). For the pH 4.0 electrolyte the nickel concentration was 1.0 M and the citrate concentration was 0.3 M. Experiments were carried out with a copper concentration of 0.004 M. Ni-Cu-γ alumina composite electrodeposition with alumina nanoparticles was conducted with varying concentrations of alumina particles (3.125 – 12.5 g/l). The alumina particles had an average diameter of 32 nm and a specific surface area reported by the manufacturer was 30-60 m²/g (Nanophase Technologies Corporation, Inc., lot# A70927-01). For the pH 8.0 electrolyte, two different copper concentrations (0.004 and 0.04 M) were tried. The nickel and citrate concentrations were maintained the same as the low pH electrolyte. The pH was increased by addition of approximately 125ml/l of 14 N ammonium hydroxide.
Different alumina concentrations (1.625-12.5 g/l) were used. The gold plating solution was from a commercial vendor (Technic, Inc., Techni Gold 25 E). The temperature of the baths was maintained at 25°C ± 0.2 with a water bath.

3.7 Characterization

Both optical and compositional analysis of the electodeposits was carried out. Scanning Electron Microscopy (SEM) and an electron microprobe (EMP) with energy dispersive X-ray spectroscopy (EDS) and wavelength dispersive X-ray spectrometers (WDS) were utilized for obtaining detailed information on the deposits. Transmission electron microscopy (TEM) was carried out to view the grain and the particle distribution in the deposit.

After deposition, the PMMA was dissolved in acetone to release the free standing microstructures. The samples were mounted in epoxy and cut using an Accutom-5 with a 356-CA cutting saw. This was then successively polished with alumina sizes of 5, 1 and 0.3 µm. A 200 Å carbon film was evaporated (Benton 502 carbon coater) on to the epoxy-mounted sample for analysis of the deposits.

The SEM (JSM-840A) was used to image the deposit surface and the microstructures X-ray elemental mapping was used to furnish the information of element distribution. An energy-dispersive x-ray detector is used for elemental mapping. To visualize the spatial distribution of each element, a series of micrographs from the same field is taken but in different modes such as back-scattered electrons, x-ray map, and secondary electrons. WDS were used to analyze the composition of the alloy with the JEOL JXA-733 microprobe, which quantitatively determines the elemental composition. Compositional analysis using a linescan with 10 µm intervals
was performed along the length of the post in the direction of the substrate using the WDS. The size of the interaction volume of the electron beam and the sample was 1 µm in diameter and the quantitation for each measurement is an average over this area.

TEM was used to verify the structure of the composite deposits and the powder itself. Specimens for the TEM were made by dispersing the alumina powder in 10% methanol in water. A drop of the suspension was placed on a holey carbon grid film and allowed to dry. Specimens of the composite films were obtained by scraping the deposit off the substrate and were prepared similarly. A JEOL TEM (Model JEM 2010) at 200 KeV and a point to point resolution of 23nm was used to produce the optical and bright-field images.

Knoop microhardness tests were performed in measuring the hardness profile of cross-sections of microposts. In the Knoop microhardness measurements, an elongated diamond pyramidal indenter is used. The angles between the long and short edges are 172.30° and 130°. This produces a parallelogram impression. The Knoop microhardness profile in the micropost was obtained from tables by measuring the length of the longer diagonal. Microhardness measurements were made with a Future-Tech, MF-100 microhardness tester with a 50 g load for local areas and duration of 20 seconds.
CHAPTER 4.

EXPERIMENTAL RESULTS

This chapter deals with the deposition of nickel copper alloys and nickel copper–alumina nanocomposites. Experimental results of the deposition into patterned recessed electrodes are presented for different pHs, current densities, duty cycles and alumina concentrations. Results of transient experiments into these recesses are reported. Rotating cylinder experiments are used to investigate the deposition process and explain observations of the deposition in the recesses. Characteristic constants of the depositing species, such as the diffusion coefficient and Tafel slopes are also extracted from experimental data.

4.1 Deep Recess Deposition

Electrodeposition by the application of a constant potential (potentiostatic) or current (galvanostatic), is most desirable because these conditions represent the lower limit in processing time. Potentiostatic deposition of elemental nickel from a sulfamate bath has been widely demonstrated by other groups\textsuperscript{100,110,132} and was confirmed experimentally. Analogously, galvanostatic DC plating (5-25 mA/cm\textsuperscript{2}) and potentiostatic DC (-0.5 to -1.5 V) plating of Ni-Cu in the recessed electrodes were attempted, and did not produce acceptable deposits at the start of deposition, deep within the recess. The deposits were non-uniform, rough and dendritic over the entire pattern. On sustained application of a constant potential or current (DC), precipitation was observed in the recess. The concentration of hydroxyl ions (OH\textsuperscript{−}), a product of the following side reactions,

\[ O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \] \hspace{1cm} (4.1)
accumulates at the electrode surface, leading to a steep increase in the local pH at the electrode surface. In addition, proton consumption via reduction further exaggerates the pH rise,

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  

The increased pH results in the formation of insoluble species of nickel and copper, which block the electrode surface and prevents further growth of the deposit. Gas evolution also leads to a loss of current efficiency, lack of deposit uniformity and increased surface roughness created by gas bubbles blocking local regions on the electrode surface. In addition, hydrogen can be included into the film and produce a more brittle and structurally weaker deposit, referred to as hydrogen embrittlement.\(^{151}\)

To overcome these challenges, a pulse scheme with long relaxation times was adopted to avoid the surface pH rise and allow the products of side reactions to diffuse out of the recess.

### 4.1.1 Pulse Parameter Selection

For a pulsing scheme to be successful, values of the applied peak currents and duty cycles must be selected judiciously. In order to determine the magnitudes of the peak currents during the on-pulse, different applied currents were studied experimentally as well as theoretically (see Chapter 5). Figure 4.1 shows the response of potential, to different step inputs in current for a pH 4.0 electrolyte. At current densities above 15 mA/cm\(^2\), the potential increases to higher magnitudes quite rapidly, consistent with a Sand’s equation-type response for diffusion controlled species. This is undesirable because it indicates the increased contribution of side reactions, which
contribute to the generation of hydroxyl ions and cause precipitation. At a value of 25 mA/cm², the potential rises to a large enough value to cause an overload of the power supply. Therefore pulses with on times less than 20 seconds and in the current density region of 5 - 15 mA/cm² were chosen for further study.

Figure 4.1 Potential responses with time for various step inputs of current densities (a) 5 mA/cm² (b) 10 mA/cm² (c) 20 mA/cm² (d) 25 mA/cm².

In choosing an appropriate duty cycle, the off time is also equally important. Therefore, the time required for the concentrations at the surface of the electrode to revert back to its initial bulk values were examined by monitoring the open circuit potential. The potential response during an off pulse, when there is no current flowing, is an indicator of the surface concentrations, according to the Nernst equation,

$$E_{rev} = E^o + \frac{RT}{nF} \ln \prod_j \frac{a_{ox,j}^{l_{ox,j}}}{a_{red,j}^{l_{red,j}}}$$

(4.4)
where $E_{rev}$ is the equilibrium potential and in the absence of displacement or corrosion reactions it is equal to the open circuit potential measured with respect to a reference potential. $E^0$ is the standard equilibrium potential, $a_{ox,j}$ and $a_{red,j}$ are the activities of the oxidized and reduced species, and $s_{ox}$ and $s_{red}$ their respective stoichiometric coefficients. The equilibrium potential is dependent upon the activities of the species, $a_{ox,i}$ and $a_{red,i}$ at the electrode surface and thus the species’ surface concentrations, while assuming unit activities for solid and gas phases.

Figure 4.2 shows the potential response for different on pulses, ranging from 5-25 seconds at a constant current pulse of 15 mA/cm$^2$. The potential response shows a decay from the end of the on pulse to its original value, within 65 seconds at most. To ensure deposition, off times greater than 70 seconds and on times of 10 seconds were chosen. This provides enough time for all species within the recess and near the electrode surface to revert back to their bulk concentrations.

On unrecessed electrodes, voltammetric experiments and polarization curves with different scan rates of potential are commonly carried out to help determine the importance and regimes of kinetic and mass-transport phenomena. A similar approach with the recessed electrodes was carried out. Figure 4.3 (a) shows the current responses for different potential scan rates ranging from 1-6 mV/s. A flat region in the polarization curve, similar to that observed in the limiting current region of copper in unrecessed electrodes is seen, but the value of this current increases with scan rate. This dependence on the scan rate shows that the deposition process is not at steady state and is indicative of a transient process. In a potential scan, a small potential step is applied at a predefined scan rate. With each incremental potential step, a
concentration gradient of the mass transport controlled species is imposed at the electrode surface. In a deep recess, with no convective effects, the concentration overpotential set up at the onset of a potential step, does not reach a steady state value before the next step. A time dependent depletion layer results and the electrodeposition process cannot attain a steady state. In other words, the sweep rates employed are too fast to obtain a steady state profile. As evidence of the transient regime, value of what appears to be a limiting current is much too high as compared to the steady state value. Theoretically one would expect to see a peak, \( i_{pk} \) (mA/cm\(^2\)), in the transient current response, with an increase in the square root of the scan rate (\( \lambda \)), (V/s) for a diffusion controlled reaction, which would be dictated by the Randles-Sevcik equation,

\[
i_{pk} = k_{ns} n^{3/2} D^{1/2} C^{1/2} \lambda^{3/2}
\]

where \( D \) (cm\(^2\)/s) is the diffusion coefficient, \( C \) (mol/cm\(^3\)) is the concentration and \( k_{ns} \) is a constant \((2.69 \times 10^5)\). Figure 4.3 (b) is a log plot of the apparent peak or limiting current \( (i_{pk}) \) versus the scan rate \( (\lambda) \). The slope of this line is not the expected value of 0.5, indicating that diffusion is not the only process occurring. The current predicted by Equation 4.5 is for a single component, while the contribution to the current in the experiment is from the superpositioning of a multicomponent system - the nickel, copper and the side reaction.

The transient nature of the deposition process holds, not only for short time frames but also for longer times due to the change of the height by the depositing metal. As more of the alloy is deposited, the thickness of the boundary layer decreases
with time, resulting in an increase of the limiting currents of the mass transport controlled reactants.

![Graph](image)

**Figure 4.2** Response of the potential to a step input of 15 mA/cm$^2$ for different on-times in a recessed electrode (a) 10 s (b) 15 s (c) 20 s (d) 25 s.

![Graph](image)

**Figure 4.3** (a) Polarization curves on a recessed electrode at different scan rates (a) 1 mV/s (b) 3 mV/s (c) 5 mV/s (d) 6 mV/s
4.1.2 Impedance Spectroscopy

The ohmic resistance between the reference electrode and the working electrode can be obtained from impedance spectroscopy. Impedance measurements also give an indication of the governing mechanism of the deposition process, such as kinetic or mass-transport control. At a fixed value of the potential of the working electrode, a sinusoidal component with a peak to peak amplitude is applied. The measured components are the magnitudes of the ac component of the current and the phase angle. In typical cases, the ohmic resistance is the real impedance measured at high frequencies, as the imaginary component of the impedance approaches zero. The Nyquist plot is a plot of the imaginary part of the impedance on the y-axis and the real part of the impedance on the x-axis. A semi-circular response represents a kinetically
controlled reaction and a straight line at an angle to the x-axis represents the dominance of mass-transport.

In unrecessed electrodes and systems with high rates of mass-transport and fast kinetics, high frequencies on the order of kHz to MHz are commonly applied. The low frequency end is usually on the order of Hz and is used to detect diffusion, which is a slower process than reaction kinetics or the double layer capacitance. An upper limit of 15 KHz was found to be the most applicable in the case of a 500 µm recess. The lower limit was set at 100 Hz. Below this frequency, the signal to noise ratio rapidly deteriorated. The amplitude of the perturbation was set at 200 mV. Too low an amplitude (5 -10 mV) results in a poor signal and generation of higher harmonic signals.

The Nyquist plot for a low pH and high pH electrolyte is shown in Figures 4.4 and 4.5. Both scans were at a potential of –2 V with an amplitude of 200 mV versus SCE in a 500 µm deep recess. The frequency was modulated between 100 Hz and 15 KHz. In both electrolytes, a straight line response indicating that mass-transport is the overall dominate process for including both Cu and Ni deposition. In order to have only copper under diffusion control the potential should be more positive. The choice of applied current for the deep recess plating was thus chosen so that the resulting potential was not as large as the impedance plots shown in Figures 4.4 and 4.5. The primary utility of the impedance plots are for the determination of the ohmic drop, $IR$. The ohmic resistance, $R$, is the point at which the imaginary part of the resistance intersects the x-axis. The resistance is normalized by the area of the electrode (Ω-cm²).
In the acidic electrolyte it was $6.5 \, \Omega\text{-cm}^2$ and in the basic electrolyte was $11.1 \, \Omega\text{-cm}^2$.

A scattering of data points in both figures is visible at the lower frequency end.

Figure 4.4 Nyquist plot of Ni-Cu alloy deposition from a pH 4.0 electrolyte at -2 V vs. SCE.

Figure 4.5 Nyquist plot of Ni-Cu alloy deposition from a pH 8.0 electrolyte at -2 V vs. SCE.
4.1.3 Ni-Cu Alloy Deposition

4.1.3.1 Low pH Deposition

Pulsed experiments were carried out for current densities of 5, 10, 15 and 25 mA/cm², having an on time of 10 seconds and an off time of 90 seconds with the low pH electrolyte. The rate of deposition at 5 mA/cm² was slow, an average deposit height of 50 microns over a 96 hour period, with a low current efficiency. At a higher current density of 25 mA/cm², precipitation occurred after a few hours of deposition and was not favorable, consistent with Figure 4.1. When the current density was 15 mA/cm², deposits of an average height of 100 microns in 96 hours were obtained. The surface was rough with considerable hydrogen evolution and precipitation after prolonged plating times. Lowering the applied current density to 10 mA/cm² proved successful.

In order to appreciate the difference between a ‘successful’ and ‘failed’ deposition, pulsed deposits carried out at 15 and 10 mA/cm² are compared. Figures 4.6 and 4.7 show microposts deposited at a current density of 15 mA/cm², having a duty cycle of 0.1. The presence of craters is evidence of hydrogen evolution and bubble formation, shown in Figure 4.6. Gas bubbles adhering to the surface block the deposition in these regions and lead to the cratering effect. Figure 4.7 shows an array of microposts, all exhibiting poor deposit formation. Figure 4.8 shows a micropost of Ni-Cu alloy electrodeposited at a current density of 10 mA/cm² for 96 hours with the same duty cycle. The average height of deposits was 100 microns and the copper concentration at the top was 2.5 wt%. The quality of deposits was better than that obtained at 15 mA/cm².
Since the low duty cycles have long deposition times, higher duty cycles were investigated. The current density was maintained at 10 mA/cm², with an on time of 10 seconds and an off time of 70 seconds, for a duty cycle of 0.125. SEM micrographs of the deposits are shown in Figure 4.9. The surface of the posts is rough, indicating a non-uniform growth process. For a thick deposit such as this, any initial roughness is propagated and may even be magnified through the growth process. The posts generated were greater than 400 µm in height. The micrograph also shows the distinctive smooth and straight sidewalls that are realized by x-ray lithography. Any variation in post width was due to the variation in size of the original mask and is not related to the exposure, developing or electrodeposition procedures. The current density lines are essentially straight and parallel to the sidewalls inside the recess. It can be assumed that no concentration gradients and hence differences in composition exist in the planes parallel to the plating surface.

![SEM micrograph of Ni-Cu deposit](image)

**Figure 4.6** Micropost of Ni-Cu at 15 mA/cm², duty cycle 0.11 from a pH 4.0 electrolyte
Figure 4.7 An array of microposts deposited at 15 mA/cm², duty cycle 0.11 from a pH 4.0 electrolyte.

Figure 4.8 Micropost of Ni-Cu alloy deposited at 10 mA/cm², duty cycle 0.11 from a pH 4.0 electrolyte.
Figure 4.9 SEM micrograph of 500 µm tall Ni-Cu posts, grown from a pH 4.0 electrolyte, deposited at a duty cycle of 0.125

Figure 4.10 shows the percentage of copper in the deposit as a function of the height of the micropost, grown at the conditions reported in the previous figure. Initially the percentage of copper is low, close to zero, representing the thick boundary layer and diffusion limitation. As the boundary layer thickness decreases, the limiting current of the mass transport limited species i.e. copper, increases and results in an increase in the percentage of copper to a maximum value of about 4 wt-%, at the mouth of the recess. The increase in concentration over the entire range is non-linear, with a larger slope of copper concentration at greater deposit heights. The scatter in the data may reflect the non-uniform growth front that developed with increasing roughness. Successful deposits, 500 µm high with the lower duty cycle of 0.1 were also grown and analyzed. These results are presented later and are used for comparisons with nanocomposite deposits, grown under identical conditions, later on in this chapter.
Figure 4.10 Weight percent of copper in the as a function of the height of the micropost, from a pH 4.0 electrolyte at 10 mA/cm² and duty cycle of 0.125

4.1.3.2 High pH Deposition

An electrolyte having the same concentration as the low pH electrolyte but with added ammonia was used to deposit the Ni-Cu alloy at pH 8.0. The current density used was 10 mA/cm², with a 10 second on and 70 second off pulse, which are the same as those used for successful depositions in the low pH electrolyte. When the compositional analysis was carried out on the cross-sections, there was no copper present in the deposit. Deposits at different current densities and duty cycles were grown and analyzed, but similar results with little or no copper were obtained. To confirm these findings, an x-ray mapping of the cross-sections was carried out and are shown in Figure 4.11.
Figure 4.11 X-ray mapping of a post grown from an ammonia electrolyte containing 1.0 M Ni and 0.004M Cu at 10 mA/cm² (a) x-ray map of nickel (b) x-ray map of copper over the same area as (a)

The nickel distribution in the post in Figure 4.11 (a) is uniform and consistent throughout the cross-section. A mapping of copper over the same post is shown in Figure 4.11 (b), indicating no copper content. As a reference point, the copper substrate is included in the analysis and is shown as the lighter area at the bottom of Figure 4.11 (b).

In the presence of ammonia, the deposition potential for the copper reduction is shifted cathodically. The cathodic shift moves the deposition of the copper to a region where the limiting current of copper is overshadowed by the kinetic deposition of nickel. This was confirmed and is represented as part of the rotating cylinder experiments later in this chapter (Section 4.1.3.2). A similar cathodic shift in the deposition potential of copper has also been reported by E. Chassaing and K. Vu. Quang³⁸ where increasing pH with ammonium hydroxide moved the deposition
potential of copper cathodically. To counter this limitation, the copper concentration was increased in the ammonia electrolyte to a higher value of 0.04 M.

An array of microposts, 500 µm high, grown from the higher copper concentration basic pH electrolyte are shown in Figure 4.12. The deposition current density was 10 mA/cm² with a 10 s on time and 70 s off time. Compositional analysis similar to the low pH deposits was carried out over a cross-section of the posts. Increased copper concentration in the electrolyte, to 0.04 M resulted in a deposit of a nickel – copper alloy. The corresponding concentration of copper is shown in Figure 4.13. The concentration gradient shows a similar shape to the one obtained from the lower pH electrolyte, with the concentration gradually increasing along the length of the micropost, indicating a diffusion controlled process. The increased copper concentration in the electrolyte results in a larger copper content in the deposit. The maximum concentration of about 20 wt-% copper is at the top of the recess where the resistance to mass transport is lowest.

Figure 4.12 Microposts grown from a pH 8.0 electrolyte with 1.0 M Ni and 0.04M Cu at 10 mA/cm² with 10 s on-time and 70 s off-time.
Two different current densities, 10 and 15 mA/cm$^2$ at the same pulse settings of 10 s on and 70 s off were used to deposit microposts. Both deposits looked similar to each other. Figure 4.14 is a comparison of the copper concentration as a function of the height of the deposit for the two current densities. The weight percent copper is represented as a weight ratio (wt-% Cu/ (wt-% Ni + wt-% Cu)). The higher current density of 15 mA/cm$^2$ exhibits a lower copper concentration than the 10 mA/cm$^2$ case until about 250 microns, beyond which the concentrations are quite similar. In both cases the gradient of copper concentration exhibits non-linearity along the deposit height. A slightly lower concentration is due to the fact that under diffusion control deep in the recess, a higher current results in increasing the concentration of the kinetically controlled nickel species and a correspondingly lower concentration of copper.
Figure 4.14 Comparison of the weight percent of copper in the as a function of the height of the micropost, from a pH 4.0 electrolyte and duty cycle of 0.125 for (a) 10 mA/cm² and (b) 15 mA/cm².

The effect of different duty cycles on the alloy composition was investigated by increasing the time of the on pulse. Figure 4.15 represents the effect of increasing on times of 10, 20 and 40 seconds for the basic pH electrolyte at 10 mA/cm², while keeping the total pulse time at 80 seconds. This corresponds to duty cycles of 0.125, 0.25 and 0.5. The initial slope of the copper gradient in the 20 seconds on-time case is not as steep as the 10 second on-time case. However, with increasing deposit heights, at about 150 µm, the copper concentrations converge to the same concentration range (10-20 wt%). A further increase in the on-time to 40 seconds results in a drop of copper concentration to a lower and constant value of about 5 wt-%. This implies that the deposition of nickel at longer on times is preferred over the copper deposition. An increase in the on-time captures two effects. One, for diffusion-controlled species, as time increases, the concentration at the surface decreases and therefore, a lower concentration of copper with increasing times of deposition can therefore be expected.
And two, a larger on-time will result in a larger pH rise at the electrode surface during the on-pulse. Since the total time was constant, and not the off-time, a longer on-time also corresponded to a shorter off-time, thus exaggerating the pH rise. A change in pH can alter kinetics, and thus the nickel reaction.

Figure 4.15 The effect of increasing on-times (a) 10 s (b) 20 s (c) 40 s for electrodeposition at 10 mA/cm² from a pH 8.0 electrolyte with the same total pulse time of 80 s.

4.1.4 NiCu Alumina Composite Deposition

4.1.4.1 Effect of pH

Nanocomposite microstructures were fabricated by the inclusion of alumina nanoparticles into the metal matrix during deposit growth from the electrolyte. Traditional composite plating baths have large concentrations (~100 g/l) of the particulate matter suspended in the electrolyte. But for a micro-patterned electrode, such as the one used in this work, a high concentration of suspended matter would
tend to agglomerate, settle and block the plating area. Low concentrations of alumina nanoparticles (1.625 - 6.25 g/l) were used to avoid this problem.

Figure 4.16 shows a SEM micrograph with the top view of microposts deposited from a Cu-γ Al₂O₃ system from a low pH electrolyte grown at 10 mA/cm² and a 0.125 duty cycle. The concentration of alumina nanoparticles was 3.125 g/l. Two different duty cycles of 0.1 and 0.125 at the same current were investigated. Figure 4.16 (b) shows a single row of the same microposts mounted in epoxy and clamped by a steel spring, which were used for the compositional analysis. The deposition was uniform across the entire cross-section of the row of posts. The topography of the composite posts appears to be smoother than the alloy posts under similar deposition conditions (see Figure 4.9). The nanoparticles act as leveling agents in a nanocomposite during both the on and off times. An improved morphology of the metal matrix with small concentrations of alumina and titania has also been reported by M. H. Fawzy et al.⁴⁴

Figure 4.16 (a) Free standing Ni-Cu-γ Al₂O₃ microposts
Figure 4.16 continued

![Image](image.png)

(b)

**Figure 4.16** (b) Row of Ni-Cu-γ Al₂O posts clamped and mounted in epoxy

An x-ray map of a cross-section of the posts is shown in Figure 4.17. A difference in contrast can be used to demonstrate the different concentrations of the elemental species. Figure 4.17 (a) shows the distribution of Ni in the post, with a few clustered regions of aluminum as seen in Figure 4.17 (c). The map shows that there is a random distribution of the alumina particles in the deposit with distinct regions of agglomeration. The same can be confirmed in the back-scattered electron image, Figure 4.17 (d) that is based on a difference in the densities of the constituent elements. The lighter regions correspond to the regions of alumina as seen in Figures 4.17 (a) and 4.17 (c). The concentration of copper in Figure 4.17 (b), on the other hand shows a thin band of higher concentration at the top of the post. This is due the external/bulk convective effects that arise from the solution agitation, which act to decrease the mass-transport boundary layer of copper and hence increase the concentration.
Figure 4.17 Mapping of the cross-section of a microposts grown at 10 mA/cm² from a pH 4.0 electrolyte at a duty cycle of 0.125 (a) x-ray map of Ni (b) x-ray map of Cu (c) x-ray map of Al
As with the nickel-copper alloy deposition, WDS compositional analysis was performed along the cross-section of the posts, to quantitatively assess the compositional distribution of the metallic species. Figure 4.18 shows the effect of alumina particles on the copper content in the deposit at a duty cycle of 0.125, and a current density of 10 mA/cm$^2$. For comparison of the metal deposition, the copper percentage in the deposit is represented as a ratio of the weight percent of copper to the total metal weight percent wt-% Cu / (wt-% Ni + wt-% Cu) in the deposit. For an alloy of Ni-Cu, this is simply the weight fraction of copper. The deposit with alumina shows a non-linear gradation in the copper concentration very similar to the alloy deposit, with on-times of 10 seconds, and off-times of 70 seconds. An important observation is that there is an increase of the copper composition in the presence of alumina nanoparticles, reflected in the greater composition of copper, as seen in the figure.
Figure 4.18 Effect of alumina on the concentration gradients of copper along the height of the recess for a deposit grown from a pH 4.0 electrolyte at 10 mA/cm² and duty cycle of 0.125.

This effect is pronounced both deep in the recess, where the effects of bulk convection are minimal and at the top of the recess. An increase in the concentration of the mass-transport limited copper by a factor of 2 or greater indicates enhancement in the diffusion of the copper through the recess. Beyond a height of 250 microns, the copper enhancement is much more dramatic. A similar copper enhancement effect was observed by using a different duty cycle of 0.1 and is shown in Figure 4.19. An increase in copper deposit concentration is observed both at the bottom and the top of the recess. Near the mouth of the recess, effects of the external fluid flow may be experienced, but at the bottom and at intermediate heights, the solution is essentially quiescent. The enhancement of the diffusion controlled component could be in part due to an improved convection, due to nanoparticles, leading to a higher copper limited current or due to an inhibition of the nickel reaction by the alumina.
Figure 4.19 Effect of alumina on the concentration gradients of copper along the height of the recess for a deposit grown from a pH 4.0 electrolyte at 10 mA/cm\(^2\) and duty cycle of 0.125.

The alumina concentration in the 0.125 duty cycle deposit as a function of height is plotted in Figure 4.20. The distribution of alumina nanoparticles in the recess is random and scattered. This is possibly due to the agglomeration that was observed in the x-ray map of the micropost (Figure 4.17) and no particular trend is evident from the figure.

A change in duty cycle, when particles were present, shown in Figure 4.21, did not significantly change the copper concentration. The deposition conditions for the analysis of deposits in Figure 4.21 are a duty cycle of 0.1 (10 s on and 70 s off) and 0.125 (10 s on and 90 s off) grown at 10 mA/cm\(^2\). Both the deposits show deposit concentrations of similar values and in the same range. The result implies that the off-times used were sufficiently long to avoid differences in pH rises at the surface. To
minimize the total time for plating, further depositions on the high pH alumina electrolyte were investigated with a total pulse time of 80 seconds and an on-pulse time of 10 seconds.

Figure 4.22 shows a SEM micrograph of an array of Ni-Cu-\(\gamma\)-alumina composite microposts electroformed by pulsing from the ammonia electrolyte at pH 8.0. The applied current density was 10 mA/cm\(^2\) with an on time of 10 seconds and off time of 70 seconds (0.125 duty cycle). The particle concentration of 3.125 g/l was at the same conditions as the low pH bath and the concentrations of the nickel, copper and citrate species were the same as the bath used for nickel-copper alloy deposition at pH 8.0. Similar to the low pH deposit, the surface morphology of the deposit appears better than the one obtained from the alloy deposition under identical conditions (Figure 4.12).

![Graph](image.png)

**Figure 4.20** Distribution of alumina along the height of the recess for a deposit grown from a pH 4.0 electrolyte at 10 mA/cm\(^2\) and duty cycle of 0.125.
Figure 4.21 Copper percentage in the micropost as a function of height for two different duty cycles grown from a low pH electrolyte at 10 mA/cm².

Figure 4.22 SEM micrograph of nickel copper alumina microposts grown at 10 mA/cm² and a duty cycle of 0.125 from a pH 8.0 electrolyte.
To qualitatively visualize the concentration gradients, a cross-section of the posts was analyzed using x-ray mapping. Figure 4.23 is a representation of the different elemental concentrations in the nanocomposite micropost. Figure 4.23 (a) shows the distribution of copper in the micropost. A graded composition of copper is observed, with increasing composition along the height of the post. This is expected due to the reduction in boundary layer thickness, as the deposit grows in the diffusion controlled regime of copper.

The greater range of copper concentrations in the deposit helps to visualize the difference in composition better than the deposits from the lower pH electrolyte (Figure 4.17) Figure 4.23 (b) is the gradient of nickel. The nickel concentration is highest at the bottom and correspondingly lower at the top (where copper is higher). Figures 4.23 (c) and 4.23 (d) are the elemental maps of aluminum and the backscattered electron image. The distribution of alumina in the post is random and agglomerated particles are present, which is similar to the lower pH electrolyte.

(a)                                                                  (b)

Figure 4.23 Mapping of the cross-section of a microposts grown at 10 mA/cm² from a pH 8.0 electrolyte at a duty cycle of 0.125 (a) x-ray map of Cu (b) x-ray map of Ni
4.1.4.2 Effect of Applied Current Density

Figures 4.24 and 4.25 compares the copper wt. ratio along the height of a representative micropost at 10 mA/cm$^2$ and 15 mA/cm$^2$, respectively, with and without the addition of nanoparticles. The ammonium electrolyte was used (high pH) and the pulsed deposition current was 10 mA/cm$^2$. The rise in concentration of copper along the height is again representative of a diffusion controlled deposition reaction. An enhancement of the copper concentration in the composite structure compared to the alloy is evident. The enhancement is primarily from the middle to the top of the recess. The copper deposit content is almost four times greater at the mouth of the recess. The particles do not affect the composition significantly at the bottom section of the recess in this case, unlike the low pH electrolyte (See Figure 4.18).
**Figure 4.24** Effect of alumina on the concentration gradients of copper, represented as weight ratios, along the height of the recess for a deposit grown from a pH 8.0 electrolyte at 10 mA/cm$^2$ and duty cycle of 0.125.

A comparison of the copper concentrations for the two different currents is shown in Figure 4.26. The deposit obtained from a current density of 15 mA/cm$^2$ has a lower copper composition than that obtained from a current density of 10 mA/cm$^2$ along the entire height of the deposit. This is due to a greater rate of nickel reaction that is expected at higher applied current densities and correspondingly lower copper compositions, which is a result of copper deposition being at its diffusional limit. The deposits for both current densities show typical non-linear compositional gradients along the height of the deposit.

Figures 4.27 and 4.28 show the concentration of alumina in the deposit grown at 10 mA/cm$^2$ and 15 mA/cm$^2$, respectively. The alumina shows diffusional control, with a concentration dependence on the boundary layer thickness. This is illustrated in
Figure 4.27 where the percentage of alumina in the deposit increases along the height of the recess to a maximum value of 5 wt-% at the top. This corresponds to a lower boundary layer thickness of the particle. The scattering of data points due to particulate agglomeration is lower in the deposit with a lower current density of 10 mA/cm$^2$ (Figure 4.27) as compared to the one at 15 mA/cm$^2$ (Figure 4.28), and as compared to the low pH deposit grown at 10 mA/cm$^2$ (Figure 4.20).

To test the reproducibility of data points, two experimental runs with the same conditions were carried out from the pH 8.0 electrolyte. The current density was 15 mA/cm$^2$, with an on-time of 10 seconds and off-time of 70 seconds. The reproducibility of the composition is illustrated in Figure 4.29, which shows the concentration profile of copper along the deposit height. Both the runs yield similar trends and range of data points.

![Figure 4.25](image-url) Figure 4.25 Comparison of copper gradients along the height of the recess for a deposits from a pH 8.0 electrolyte, with and without alumina at 15 mA/cm$^2$ and duty cycle of 0.125.
Figure 4.26 Comparison of the weight ratios of copper along the height of the micropost for two different applied current densities (a) 10 mA/cm² (b) 15 mA/cm²

Figure 4.27 The gradient of alumina concentration along the height of the micropost, grown from a pH 8.0 electrolyte at 10 mA/cm² and a duty cycle of 0.125
Figure 4.28 The gradient of alumina concentration along the height of the micropost, grown from a pH 8.0 electrolyte at 15 mA/cm² and a duty cycle of 0.125.

Figure 4.29 The gradient of copper concentration along the height of the micropost, grown from a pH 8.0 electrolyte at 15 mA/cm² and a duty cycle of 0.125 for two separate experimental runs.
4.1.4.3 Effect of Alumina Concentration

Figure 4.30 is a demonstration of the effect of alumina concentration in the electrolyte on the copper concentration obtained in the deposit. All data points were obtained at a duty cycle of 0.125 and an applied current of 10 mA/cm². At the lowest alumina concentration (1.625 g/l), there is no apparent effect of the alumina on the copper deposition. By increasing the concentration of alumina, from 1.625 to 6.25 g/l in the electrolyte, a clear trend of increasing copper concentrations is evident, with the largest particle concentration providing the greatest enhancement. This implies a direct co-relation between the particle concentration in the electrolyte and enhancement of copper. The increased amounts of particulates in the bath, act to increase the convective effect experienced within the recess and lead to greater limiting currents of copper and corresponding higher concentrations in the deposit. Increasing the concentration of the particulates to concentrations about 20 g/l, prove to be difficult due to the problems associated with sedimentation, blockage and poor deposit structure.

The alumina concentration along the height of the micropost is shown in Figure 4.31. For clarity, only the alumina concentrations of 3.125 g/l and 6.25 g/l are compared. Increasing alumina concentrations along the height of the deposit is indicative of mass-transport dependence of alumina on the boundary layer thickness. The higher alumina concentration in the electrolyte results in a higher alumina concentration (from a few percent to over 200%) in the deposit, with both the gradients showing diffusional control and scattering of data points due to agglomeration.
Figure 4.30 The effect of increasing alumina concentrations in the electrolyte on the concentration of copper in the deposit (a) 0 g/l Al₂O₃ (b) 1.625 g/l Al₂O₃ (c) 3.125 g/l Al₂O₃ (d) 6.25 g/l Al₂O₃

Figure 4.31 The effect of increasing alumina concentrations in the electrolyte on the concentration of alumina in the deposit (a) 3.125 g/l Al₂O₃ (b) 6.25 g/l Al₂O₃
Further confirmation of an enhancement of the diffusion-limited species may be obtained by a study of the Cottrellian current transient curves, when subjected to a pulse in the applied potential in the recess. The pulse is applied to a recessed electrode without any deposit at the bottom, so that the diffusion boundary layer can be approximated by the recess depth (500 µm). Figure 4.32 shows the current response in the presence of alumina nanoparticles and without, for a pulse of –1V, which is in the diffusion controlled regime for copper. The curves show similar shapes, a rapid decay of the current at shorter times, followed by an approach to steady state at longer times. In the electrolyte containing nanoparticles, the steady state current that is approached is larger than that without any nanoparticles by a factor of 2 or greater.

**Figure 4.32** Current decay curves for an applied –1V step with and without alumina nanoparticles in a pH 4.0 electrolyte.
Figure 4.33 is a similar experiment carried out on the higher pH electrolyte, with and without particles, at an applied potential of –2V versus SCE. The higher polarization needed is because of the shift of the deposition potential previously discussed. The shape of the curves and the effect of the alumina nanoparticles is similar to the curves obtained from the low pH electrolyte, with the alumina particles, tending to increase the transient current. The higher magnitudes of the transient current indicate a greater rate of reaction in the presence of the nanoparticles for Cu and Ni, since the deposit concentration did not change at the bottom of the recess.

![Current decay curves for an applied –1V step with and without alumina nanoparticles in a pH 8.0 electrolyte](image)

**Figure 4.33** Current decay curves for an applied –1V step with and without alumina nanoparticles in a pH 8.0 electrolyte

### 4.1.5 Growth Rates

In deep recess plating, the current efficiency and therefore the growth rates of the deposits are not constant throughout the growth process. For example, deep within the recess, the efficiency is low and at the mouth of the recess, the efficiency and rate...
is higher. To estimate the growth rate or the efficiency of the deposition, it is possible to measure the height of the deposit every few hours and measure the growth rate. This is not practical in the setup used without removal of the PMMA and destroying the sample. After 8 days the deposits, both with and without particles reached the surface of the recess, and produced mushroom-like deposits at the recess mouth (overplate). This does not provide a quantitative measure of current efficiency in the recess. Qualitatively, an average growth rate may be estimated from the total height of the deposit and the total time taken for deposits that were not overplated. The deposit heights, and growth rates and times are listed in Table 5.1. Some general trends may be ascertained. The growth rate of a deposit from a composite electrolyte is higher than the alloy irrespective of pH. The alloy growth rates don’t vary significantly with pH, but the composite growth rate is greater for the higher pH electrolyte. The rates of deposit growth with increasing alumina show no clear trend. The time of deposition is lower for higher currents and larger duty cycles, as expected. These growth rates obtained can only be used qualitatively.

**Table 5.1** Growth conditions and times for the various deposits in deep recesses.

<table>
<thead>
<tr>
<th>Current density (mA/cm²)</th>
<th>Electrolyte</th>
<th>pH</th>
<th>Duty Cycle</th>
<th>Final height (µm)</th>
<th>Time</th>
<th>Growth rate µm/day</th>
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<tbody>
<tr>
<td>15</td>
<td>Alloy</td>
<td>8.0</td>
<td>0.125</td>
<td>520</td>
<td>7 days 10 hours</td>
<td>70.11</td>
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<tr>
<td>15</td>
<td>Composite (3.125 g/l)</td>
<td>8.0</td>
<td>0.125</td>
<td>580</td>
<td>7 days 1 hour</td>
<td>82.36</td>
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<td>10</td>
<td>Alloy</td>
<td>4.0</td>
<td>0.125</td>
<td>400</td>
<td>8 days 15 hours</td>
<td>46.38</td>
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Table 5.1 continued

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<tr>
<td>10</td>
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<td>4.0</td>
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<td>480</td>
<td>8 days 1 hours</td>
<td>59.25</td>
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<td>0.125</td>
<td>410</td>
<td>8 days 2 hours</td>
<td>50.00</td>
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<tr>
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<td>Composite (3.125 g/l)</td>
<td>8.0</td>
<td>0.125</td>
<td>600</td>
<td>7 days 23 hours</td>
<td>75.20</td>
</tr>
<tr>
<td>10</td>
<td>Composite (1.625 g/l)</td>
<td>8.0</td>
<td>0.125</td>
<td>495</td>
<td>8 days 4 hours</td>
<td>60.61</td>
</tr>
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<td>10</td>
<td>Composite (6.25 g/l)</td>
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<td>0.125</td>
<td>350</td>
<td>5 days 6 hours</td>
<td>66.6</td>
</tr>
<tr>
<td>10</td>
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<td>0.25</td>
<td>515</td>
<td>6 days 2 hours</td>
<td>84.65</td>
</tr>
<tr>
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<td>Alloy</td>
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<td>0.5</td>
<td>560</td>
<td>5 days 11 hours</td>
<td>102.60</td>
</tr>
</tbody>
</table>

4.2 RCE Deposition

This section deals with the experiments conducted on rotating cylinder electrodes. Results of polarization curves, partial currents of metal species, side reactions and current efficiencies are presented for both the nickel-copper alloy and nickel-copper-γ alumina electrolytes at pH 4.0 and 8.0. Comparisons of the electrolytes with and without alumina yields information about the effect of alumina on the metal deposition.
4.2.1 Ni-Cu Alloy Polarization Curves

4.2.1.1 Low pH Deposition

RCE experiments were conducted to complement the data obtained from the recessed electrodes and to better understand the deposition process. Figure 4.34 shows the current-potential relationship as a function of rotation rate of the cylinder electrode, when the copper concentration was 0.004 M. The scan rate used was 5 mV/s. The polarization curves exhibit a distinct flat region corresponding to the diffusion-limited region of copper and a steeper region, which corresponds to the region of nickel deposition. The region governed by the mass transport of Cu\(^{2+}\) ions is seen in the potential range of –0.5 V to –0.65 V versus SCE. The reduction of the dissolved oxygen, given by the reaction, \(O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-\), occurs at a potential of 0.401 V vs. NHE was eliminated by bubbling nitrogen into the solution to displace oxygen.

The thickness of the diffusion layer of a rotating cylinder electrode as a function of the rotation rate, \(\omega\) is given by the Eisenberg equation\(^{139}\), where the diffusion boundary layer thickness \(\delta\) (cm) is proportional to the rotation rate, \(\omega\) (rpm) to the -0.7 power as

\[
\delta = 99.62 \times d^{-0.4} \nu^{0.344} D^{0.356} \omega^{-0.7}
\]  

(4.6)

where \(d\) is the diameter of the RCE (cm), \(\nu\) is the kinematic viscosity, \(D\) is the diffusion coefficient (cm\(^2\)/s). Equation 4.7 relates the limiting current to the boundary layer thickness as
\[ i_{\text{lim}} = \frac{nFDC^b}{\delta} \]  

(4.7)

Here \( n \) is the number of electrons, \( F \) the faradays constant and \( C^b \) is the bulk concentration of the species. From the two Equations (4.6 and 4.7) and the data in Figure 4.34, a variation of the rotation rate yields the diffusion coefficient of copper as determined from the slope in Figure 4.35. The relationship between the limiting current and \( \omega^{0.7} \) is linear, with the slope yielding the value of the diffusion coefficient, \( 1.25 \times 10^{-6} \ \text{cm}^2/\text{s} \). This relatively low diffusion coefficient is consistent with a complexed Cu-citrate reactant, as proposed by Podlaha et al. \(^{22}\)

![Figure 4.34](image)

**Figure 4.34** Polarization curves at different rotation rates on a RCE electrode from an electrolyte at pH 4.0.
Figure 4.35 Plot of the limiting current versus $\omega^{0.7}$ for a RCE electrode from a pH 4.0 electrolyte.

4.2.1.2 High pH Deposition

A similar set of experiments was attempted on an ammonia electrolyte, with 0.004 M copper. As discussed in section (4.1.3.2) for the recessed electrode, deposition of copper was hindered due to the cathodic shift observed due to the presence of ammonia in the electrolyte. Figure 4.36 shows the comparison of polarization curves at 1000 rpm for electrolytes at pH 4.0 and 8.0. The potential for the deposition is shifted to more cathodic values in the presence of ammonia. The absence of a flat defining region for mass-transport limited copper indicates a shift of the copper deposition more negative to the start of the nickel deposition.

By increasing the copper concentration in the electrolyte from 0.004 to 0.04M, the copper limiting current density and kinetic current density is increased. Figure 4.37 shows a comparison of the polarization curves obtained on a RCE, at a rotation rate of 1000 rpm for the two different copper concentrations used. The magnitude of the
current for the 0.04 M copper electrolyte is larger compared to the 0.004 M copper curve in the potential range of -0.5 to -1.0 V. There is no characteristic limiting current observed since it is overshadowed by the Ni reduction current. Codeposition of nickel and copper is thus possible for the 0.04 M Cu electrolyte in the range of −0.5 to −1.25 V vs. SCE.

Figure 4.38 shows the polarization curves obtained for a copper concentration of 0.04 M at different rotation rates. The limiting current region for copper deposition varies with rotation rate and therefore accounts for the change in the total current density. The increasing magnitude of the current with increased rotation rates indicates that the deposition in the potential range more negative than −0.7 V vs. SCE is influenced by mass transport. Since the copper limiting current density cannot be determined explicitly from this data the diffusion coefficient cannot be readily determined by inspection from the polarization curves.

Figure 4.36 Comparison of the polarization curves at 1000 rpm from 1 M Ni, 0.004 M Cu. for (a) pH 4.0 and (b) pH 8.0
Figure 4.37 Comparison of the polarization curves at 1000 rpm from a pH 8.0 electrolyte with 1 M Ni and (a) 0.004 M Cu (b) 0.04 M Cu

Figure 4.38 Comparison of the polarization curves at different rotation rates from a pH 8.0 electrolyte with 1 M Ni 0.04 M Cu (a) 800 rpm (b) 1000 rpm (c) 1500 rpm
4.2.2 Ni-Cu-\(\gamma\)-Al\(\text{2}O\text{3}\) Composite Deposition

A study of the effect of alumina concentration on the nickel-copper-alumina nanocomposite deposition from both the low and high pH electrolytes is carried out. Figure 4.39 shows the effect of alumina on the polarization curves in an electrolyte at pH 4.0 at a rotation rate of 1000 rpm. The polarization curves show a shift in the cathodic direction upon addition of alumina nanoparticles from 3.125 to 12.5 g/l. All the curves exhibit a distinct flat region corresponding to the diffusion-limited region of copper, irrespective of alumina concentration. The steeper region of the curve corresponds to the region of nickel deposition and \(H_2O\) decomposition. The most significant observation is in the kinetic Ni section of the curves. The addition of nanoparticles results in a shift of the Ni portion of the curve to more cathodic potentials and indicates inhibition of the nickel side reaction. This shift shows a dependence on alumina concentration in the electrolyte, with the larger concentration of alumina causing the greatest cathodic shift of nickel.

Figure 4.40 shows the effect of increasing amounts of alumina (3.125 to 12.5 g/l) on the basic pH electrolyte. Unlike the effect on the lower pH electrolyte, increasing concentrations of alumina particles do not appear to shift or alter the polarization curves of the basic pH electrolyte, with all the curves almost overlapping each other. Therefore, the sum of the electrochemical reaction rates have not changed significantly with added alumina to the electrolyte. To determine the effect of alumina on the individual metal side reactions and the current efficiency, the partial currents of each contributing component - nickel, copper and the side reactions are considered individually.
Figure 4.39 Polarization curves carried out with and without alumina nanoparticles from a pH 4.0 electrolyte at \( \omega = 1000 \) rpm and varying alumina concentrations (a) 0 g/l (b) 3.125 g/l (c) 6.25 g/l (d) 12.5 g/l

Figure 4.40 Polarization curves carried out with and without alumina nanoparticles from a pH 8.0 electrolyte at \( \omega = 1000 \) rpm and varying alumina concentrations (a) 0 g/l (b) 3.125 g/l (c) 6.25 g/l (d) 12.5 g/l
4.2.3 Effect of Al₂O₃ on Partial Currents and Current Efficiencies

Metal partial current densities \( (i_{\text{metal}}) \) are calculated by using Faraday’s law. The partial current densities were deconvoluted from the total current by taking the weight of the deposit and the composition into account

\[
i_{\text{metal}} = -n \cdot F \cdot \frac{m_{\text{deposit}} \cdot W_{\text{metal}}}{a \cdot t \cdot M_{\text{metal}}}
\]

\( n \) is the valence of the metal ion, \( F \) is the Faraday constant, \( m_{\text{deposit}} \) is the mass of the deposit, \( W_{\text{metal}} \) is the weight percent of the metal in the alloy deposit, \( a \) is the surface area of the deposit, \( t \) is the time duration of the deposition and \( M_{\text{metal}} \) is the molecular weight of the metal.

Figure 4.40 shows a comparison of the Ni partial current density with and without particles at pH = 4.0. The nickel reaction rate is kinetically controlled in this range. A dramatic shift of the Ni partial current density to more cathodic potentials in the presence of alumina is observed. This inhibition of the nickel rate is consistent with the shift in the kinetic region of the polarization curve, with increasing particle concentration as seen in Figure 4.39. Since the slopes of the two nickel partial current densities are similar, the inhibition mechanism is expected to be due to surface site blocking by the alumina particles and not an alteration of the nickel reaction mechanism. This inhibition of the nickel partial current contributes partially to the enhancement of the copper concentration observed at the bottom in the recessed electrode. This is consistent with the findings of Webb and Robinson⁸² who also reported an inhibition of nickel from a nickel and alumina system from a sulfamate electrolyte.
To determine the transfer coefficient, $\alpha$ and the exchange current density, $i_0$ of the nickel reaction, a Tafel plot, of nickel was examined. The plot of $\log_{10}(i_{Ni})$ versus $E$, from the Ni-Cu electrolyte, shown in Figure 4.41, is linear and yields a slope of $-5.22 \pm 0.33 \text{ V}^{-1}$ with an intercept of $-3.59 \pm 0.281$. From the Tafel equation for the cathodic reaction

$$\ln i_c = \ln i_0 + \left( \frac{\alpha nF \eta}{RT} \right)$$  \hspace{1cm} (4.9)\

the value of $\alpha$ was calculated to be 0.154 and $i_0$ was $0.25 \times 10^{-5}$ mA/cm$^2$. These quantify the kinetically controlled nickel reaction. The Tafel slope of the nickel side reaction with alumina is shown in Figure 4.42. The value of the slope is $-5.064 \pm 0.50$ V$^{-1}$ and the value of the intercept is $4.489 \pm 0.55$. This yields the value of $\alpha$ to be 0.149 and $i_0$ was $3.25 \times 10^{-5}$ mA/cm$^2$. Both values of $\alpha$ and $i_0$ with and without alumina are similar, indicating no change in the kinetic rate of nickel deposition, only a shift of deposition potential.

Figure 4.43 is a comparison of the plots of the partial currents of Cu with and without alumina nanoparticles, over the entire range of currents. A limiting current of copper can be seen clearly at 1 mA/cm$^2$ for the electrolyte without alumina. The copper current density is slightly suppressed in the presence of alumina, but, not as dramatically as the nickel reaction. The net resulting composition is shown Figure 4.44, where the weight percent copper in the deposit with particles is lower than that obtained without particles. At low current densities, the percentage of copper is higher than at higher current densities. Above a current density of 35 mA/cm$^2$, the compositions of copper converge.
Figure 4.40 Plot of partial currents of nickel reactions with and without alumina from a pH 4.0 electrolyte, on a RCE at $\omega = 1000$ rpm.

Figure 4.41 Tafel plot of the nickel partial current density from a nickel copper electrolyte at pH 4.0
Figure 4.42 Tafel plot of the nickel partial current density from a Ni-Cu-γ Al₂O₃ electrolyte at pH 4.0

Figure 4.43 Plot of partial currents of copper side reactions with and without alumina from a pH 4.0 electrolyte, on a RCE at ω = 1000 rpm.
Figure 4.44 Comparison of the wt-% copper in the deposit as a function of the applied current density obtained from a pH 4.0 electrolyte, with and without alumina at 1000 rpm.

Figure 4.45 and 4.46 shows the effect of alumina on the partial current of the nickel species a high pH electrolyte. Figure 4.46 shows the partial current of the nickel species as a function of the measured potential versus SCE in order to compare with the low pH case. The kinetically controlled nickel reaction, increases with increasing applied current densities.

Unlike the low pH electrolyte, the presence of alumina in the high pH electrolyte, with ammonia shows no significant effect on the nickel deposition reaction. The slopes of the two deposition curves are almost the same and overlap each other, seen in Figure 4.45, indicating that the rate of nickel deposition is unaffected by the presence of alumina. This effect is not readily apparent in Figure 4.46, where the x-axis represents the measured potential versus SCE, since the potential of the electrode surface with the ammonia electrolyte varies with time at large negative potentials.
Figure 4.45 Plot of partial currents of nickel side reactions with and without alumina from a pH 8.0 electrolyte versus the applied current density, on a RCE at $\omega = 1000$ rpm.

Figure 4.46 Plot of partial currents of nickel side reactions with and without alumina from a pH 8.0 electrolyte versus the measured potential, on a RCE at $\omega = 1000$ rpm.
The nickel reaction is kinetically controlled. A Tafel plot of the nickel partial current, similar to the pH 4.0 electrolyte, yields information about the exchange current density, $i_0$ and the transfer coefficient, $\alpha$. Figure 4.47 is a Tafel plot of the log of the partial current density of nickel. The slope of the line is $-4.31 \pm 0.62 \text{ V}^{-1}$ and the intercept is $-4.17 \pm 0.66$. This yields a value of 0.127 for $\alpha$ and $6.79 \text{ e}^{-5} \text{ mA/cm}^2$ for the exchange current density, $i_0$. The order of the exchange current densities and transfer coefficients are similar for both the low and high pH.

![Tafel plot of the nickel partial current density from a Ni-Cu-$\gamma$ Al$_2$O$_3$ electrolyte at pH 8.0](image)

**Figure 4.47** Tafel plot of the nickel partial current density from a Ni-Cu-$\gamma$ Al$_2$O$_3$ electrolyte at pH 8.0

Figures 4.48 and 4.49 show the comparison of the partial current densities of the copper deposition reaction in the ammonia electrolytes, with and without alumina as a function of the total applied current density and the measured potential, respectively. The deposition of copper indicates a mass-transport limited reaction, where the partial current density is invariant over the range of applied current...
densities, except at the lower current end, where it is kinetically controlled. This behavior is similar to the low pH electrolyte. The limiting current density of copper, both with and without alumina appears at a value of about 5mA/cm². The alumina does not affect the copper deposition in either the kinetic or the mass transport regimes. This effect is not readily apparent in Figure 4.49, where the partial current density of copper is plotted against the measured potential. This is because the potential at a constant current density varies over time and is a function of the surface concentration of the various species present, which, may change as the surface of the electrode changes during the deposition process. The applied current, however, is controlled by the galvanostat and is hence constant.

The partial currents of copper translate into its weight percent in the deposit. The comparison of the weight percent of copper, with and without alumina, as a function of the applied current density is seen in Figure 4.50. The percentage of copper in the deposit is not affected significantly by the presence of alumina in the electrolyte. The weight percent copper drops from a predominantly copper rich region (greater than 50 wt-%), at lower current densities (less than 10 mA/cm²) to a region of lower copper concentration at higher current densities. This behavior is similar to the low pH electrolyte, but with different copper concentrations in the deposit, which represent the higher copper composition of the ammonia electrolyte. The drop is due to the increased kinetically controlled nickel reaction rate with increasing applied current density, and the copper having attained its limiting current density. Unlike in a low pH electrolyte, the presence of alumina does not have a significant effect on the metal side reactions in the high pH electrolyte.
Figure 4.48 Plot of partial currents of copper side reactions with and without alumina from a pH 8.0 electrolyte versus the applied current density, on a RCE at $\omega = 1000$ rpm.

Figure 4.49 Plot of partial currents of copper side reactions with and without alumina from a pH 8.0 electrolyte versus the measured potential, on a RCE at $\omega = 1000$ rpm.
The incorporation of alumina in the alloy matrix from a pH 4.0 electrolyte can be seen in Figure 4.51, where the percent alumina is plotted as a function of applied current density. The percentage incorporation is low, about 1 wt-% and shows no dependence on the plating current density. This corresponds to a diffusion controlled particle boundary layer and mass transport limited deposition. The weight percent alumina in the deposit from the ammonia electrolyte is shown in Figure 4.52. Similar to the low pH electrolyte, the composition of alumina does not vary significantly as a function of the applied current density and shows a relatively constant composition, at about 3 wt-% indicating a diffusion controlled deposition mechanism for the nanoparticles. The low weight percent incorporation of alumina reflects the low alumina concentration in the electrolyte.

Figure 4.50 Comparison of the wt-% copper in the deposit as a function of the applied current density obtained from a pH 8.0 electrolyte, with and without alumina at 1000 rpm.
Figure 4.51 The wt-% alumina in the deposit as a function of the applied current density obtained from a pH 4.0 electrolyte at 1000 rpm.

Figure 4.52 The wt-% alumina in the deposit as a function of the applied current density obtained from a pH 8.0 electrolyte, at 1000 rpm.
The current efficiency ($\eta$) is the ratio of current density that is used to electrodeposit the metals compared to the total applied current density, and is usually expressed on a percent basis

$$\eta(\%) = \frac{\sum i_{metal}}{i_{total}} \times 100$$

(4.10)

The side reaction current density ($i_{side}$) is the difference between the total current density ($i_{total}$) and the sum of all the metal partial current densities ($\sum i_{metal}$).

$$i_{side} = i_{total} - \sum i_{metal}$$

(4.11)

Figure 4.53 shows the current efficiencies of the pH 4.0 electrolyte with and without alumina nanoparticles plotted as a function of the applied current density. The loss of efficiency can be accounted for by the side reactions, given by Equations 4.1, 4.2 and 4.3, and contributes to the total applied current density. The efficiency for the electrolyte with alumina is lower than that of the electrolyte without it. At lower current densities the current efficiency is below 50% and increases with an increase in the applied current density. The efficiency appears to reach a maximum at about 40 mA/cm$^2$. The efficiency was calculated for a constant charge density of 7.32 Ampere-second/cm$^2$.

The partial current densities of the side reactions in a pH 4.0 electrolyte, with and without alumina are plotted in Figure 4.54. The contribution of the side reaction to the total current density, in the alumina electrolyte is higher than that of the electrolyte without alumina, especially at more negative potentials. This accounts for the lower current efficiency of the alumina electrolyte in comparison to the electrolyte without alumina at pH 4.0
Figure 4.53 Comparison of the current efficiency as a function of the applied current density from a pH 4.0 electrolyte, with and without alumina at 1000 rpm.

Figure 4.54 Comparison of the contribution from the side reaction versus potential from a pH 4.0 electrolyte, with and without alumina at 1000 rpm.
Similar to the low pH electrolytes, RCE experiments on the pH 8.0 electrolyte were carried out. Figure 4.55 shows the current efficiency of the high pH electrolyte with and without alumina nanoparticles. For lower current densities, the alumina electrolyte has a lower current efficiency than the electrolyte without any alumina. Beyond about 20 mA/cm$^2$, the current efficiencies are similar for both the electrolytes, with and without alumina, and higher than the low current end.

![Figure 4.55](image)

**Figure 4.55** Comparison of the current efficiency as a function of the applied current density from a pH 8.0 electrolyte, with and without alumina at 1000 rpm.

Figure 4.56 is a representation of the side reaction as a function of the applied current density in the high pH electrolyte both with and without alumina. Figure 4.57 is the side reaction as a function of the observed potential. The side reaction at lower current densities (below 10 mA/cm$^2$) is slightly higher in the case of the electrolyte with alumina, which contributes to a lower current efficiency. At higher current
densities, both the current efficiency and the contribution of the side reaction are similar in both the electrolyte with and without alumina.

**Figure 4.56** Comparison of the current efficiency as a function of the applied current density from a pH 8.0 electrolyte, with and without alumina at 1000 rpm.

**Figure 4.57** Comparison of the contribution from the side reaction as a function of the measured potential from a pH 8.0 electrolyte, with and without alumina at 1000 rpm.
4.3 TEM Analysis

Figure 4.58 (a) is a TEM image of the $\gamma$-Al$_2$O$_3$ particles. The picture clearly shows spherical alumina particles and a wide distribution of sizes (5-150 nm). Figure 4.58 (b) is the Same Area Electron Diffraction (SAED) pattern, from a single $\gamma$-Al$_2$O$_3$ particle. The electron diffraction pattern is indexed and shown on the same figure and represents the crystalline pattern of alumina for an electron beam direction of [110].

Figure 4.59 (a) is a TEM image of the Ni-Cu-$\gamma$-Al$_2$O$_3$ matrix and Figure 4.59 (b) is the SAED pattern. This was obtained from a Ni-Cu-$\gamma$-Al$_2$O$_3$ composite deposit grown from a pH 4.0 electrolyte, at 10 mA/cm$^2$, on a RCE at 1000 rpm. Figure 4.59 (a) clearly shows spherical alumina particles embedded in the alloy matrix. The grain size is of the metal matrix is about 100 nm. The electron diffraction pattern in Figure 4.59 (b) is an effect of superpositioning of several diffraction patterns of both the alloy and the particle and displays no regular orientation.

(a)

Figure 4.58 (a) TEM image of Al$_2$O$_3$ particles


Figure 4.58 continued

(b) Electron diffraction pattern of a single particle over the same area.

Figure 4.58 (b) Electron diffraction pattern of a single particle over the same area.

(a) TEM image of a Ni-Cu-\(\gamma\)-Al\(_2\)O\(_3\) composite deposit grown from a pH 4.0 electrolyte, at 10 mA/cm\(^2\), on a RCE at 1000 rpm

Figure 4.59 (a) TEM image of a Ni-Cu-\(\gamma\)-Al\(_2\)O\(_3\) composite deposit grown from a pH 4.0 electrolyte, at 10 mA/cm\(^2\), on a RCE at 1000 rpm
4.4 Microhardness

The microposts from the pH 8.0 electrolyte, with and without alumina were analyzed for gradients in microhardness, associated with gradients of compositions along the height of the micropost. The Knoop microhardness test results are shown in Figure 4.60. No significant variations or trends are visible for either the Ni-Cu alloy or Al<sub>2</sub>O<sub>3</sub> deposits, along the height of the posts. The deposits at 15 mA/cm<sup>2</sup> (650-700) had a greater hardness than those at 10 mA/cm<sup>2</sup> (500-650), due to the higher percentage of nickel in the deposit, which is harder than copper. The presence of alumina increases the hardness only slightly, for the deposits at 15 mA/cm<sup>2</sup> because of the low percentage of alumina in the deposit. The alloy deposits from a higher duty cycle of 0.25 yields microposts with a slightly lower microhardness than those at a duty cycle of 0.125. The microhardness of both the alloy and composite microposts
were higher than those reported by Wang\textsuperscript{100} who reported hardness Knoop hardness values of about 400 for nickel, and 400-550 for nickel-alumina microposts.

**Figure 4.60** Knoop hardness of deposit along the height of microposts grown from a pH 8.0 electrolyte (a) Ni-Cu-\(\gamma\)-Al\(_2\)O\(_3\) composite micropost at 15 mA/cm\(^2\) (b) Ni-Cu alloy micropost at 15 mA/cm\(^2\) (c) Ni-Cu alloy post at 10 mA/cm\(^2\), duty cycle 0.125 (d) Ni-Cu alloy post at 10mA/cm\(^2\), duty cycle 0.25.
CHAPTER 5.

MODEL DEVELOPMENT

In this chapter, finite difference numerical models are developed to simulate the nickel copper alloy and nickel copper alumina nanocomposite depositions under steady state conditions, and under non-steady state conditions. The effect of alumina on the metal deposition partial currents and side reactions is simulated by using a surface coverage model. On the unrecessed electrodes a transient model taking into account the time dependence of concentration is developed. The rise of surface pH, concentration gradients and buffering effects of the complexing agents are explained by the non-steady state model.

5.1 Steady State Deposition

5.1.1 Homogeneous Chemical Equilibrium

In the citrate electrolyte, at pH 4.0 the chemical equilibria of Ni$^{2+}$, Cu$^{2+}$, Na$^{+}$, SO$_4^{2-}$, CuSO$_4$, NiSO$_4$, NaSO$_4$ bisulfate (HSO$_4^-$), citrate (Cit$^{3-}$), hydrogen citrate (Hcit$^{2-}$), nickel citrate (NiCit$^-$), copper citrate (CuCit$^-$), sodium citrate (Na$_3$Cit), H$_2$O, H$^+$ and OH$^-$ are represented by Equations 1-9, listed in Table 5.1. The equilibrium constants 142-145, 152 ($K_j$) of these reactions are tabulated in Table 5.2.

The total concentrations of nickel, copper, citrate, sodium, and sulfur are known and given by their mass balance relations (Equations 5.10 – 5.15). The nickel and copper concentrations are the sum of the metal-citrate complex, free metal ions and metal sulfates. The citrate concentration is given by the uncomplexed free citrate, the metal-citrate species, the undissociated sodium citrate and the hydrogen citrate. The sodium ion concentration is determined by the sodium citrate, free sodium ions and
sodium sulfate. The hydrogen ion concentration is given by the solution pH (Equation 5.6). The fifteen equations thus obtained were solved simultaneously for all fifteen variables \((\text{Ni}^{2+}, \text{Cu}^{2+}, \text{Na}^{+}, \text{SO}_4^{2-}, \text{CuSO}_4, \text{NiSO}_4, \text{NaSO}_4, \text{HSO}_4^-, \text{Cit}^3-, \text{Hcit}^2-, \text{NiCit}^-, \text{CuCit}^-, \text{Na}_3\text{Cit}, \text{H}^+ \text{ and OH}^-)\) on Mathematica (Version 4.1).

**Table 5.1** Chemical Equilibria associated with the low pH electrolyte

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu}^{2+} + \text{Cit}^3- \rightleftharpoons \text{CuCit}^-)</td>
<td>1</td>
</tr>
<tr>
<td>(\text{Cu}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CuSO}_4)</td>
<td>2</td>
</tr>
<tr>
<td>(\text{Ni}^{2+} + \text{Cit}^3- \rightleftharpoons \text{NiCit}^-)</td>
<td>3</td>
</tr>
<tr>
<td>(\text{Ni}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{NiSO}_4)</td>
<td>4</td>
</tr>
<tr>
<td>(3\text{Na}^{+} + \text{Cit}^3- \rightleftharpoons \text{Na}_3\text{Cit})</td>
<td>5</td>
</tr>
<tr>
<td>(\text{Hcit}^2- \rightleftharpoons \text{Cit}^3- + \text{H}^+)</td>
<td>6</td>
</tr>
<tr>
<td>(\text{Na}^{+} + \text{SO}_4^{2-} \rightleftharpoons \text{NaSO}_4^-)</td>
<td>7</td>
</tr>
<tr>
<td>(\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-})</td>
<td>8</td>
</tr>
<tr>
<td>(\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+)</td>
<td>9</td>
</tr>
</tbody>
</table>

**Table 5.2** Equilibrium constants of the chemical equilibria in Table 5.1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant</th>
<th>Equation No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{K}<em>{\text{CuCit}^-} = \frac{C</em>{\text{Cu}^{2+}} C_{\text{Cit}^3-}}{C_{\text{CuCit}^-}})</td>
<td>(6.329 \times 10^{-18} \text{ mol cm}^{-3})</td>
<td>5.1</td>
</tr>
<tr>
<td>(\text{K}<em>{\text{CuSO}<em>4} = \frac{C</em>{\text{Cu}^{2+}} C</em>{\text{SO}<em>4^{2-}}}{C</em>{\text{CuSO}_4}})</td>
<td>(4.46 \times 10^{-6} \text{ mol cm}^{-3})</td>
<td>5.2</td>
</tr>
</tbody>
</table>
Table 5.2 continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Expression</th>
<th>Value</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{NiCit} = \frac{C_{Ni^{2+}}C_{Cit^{-}}}{C_{NiCit}}$</td>
<td>$5.025 \times 10^{-18}$ mol cm$^{-3}$</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>$K_{NISO_4} = \frac{C_{Ni^{2+}}C_{SO_4^{2-}}}{C_{NISO_4}}$</td>
<td>$3.98 \times 10^{-6}$ mol cm$^{-3}$</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>$K_{Na_3Cit} = \frac{C_{Na^{+}}C_{Cit^{-}}}{C_{Na_3Cit}}$</td>
<td>$3.98 \times 10^{-10}$ mol$^3$ cm$^{-9}$</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>$K_{HCl_2^2} = \frac{C_{H^+}C_{Cit^{-}}}{C_{HCl_2^2}}$</td>
<td>$1.25 \times 10^{-9}$ mol cm$^{-3}$</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>$K_{NaSO_4} = \frac{C_{Na^{2+}}C_{SO_4^{2-}}}{C_{NaSO_4}}$</td>
<td>$1.99 \times 10^{-4}$ mol cm$^{-3}$</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>$K_{HSO_4^-} = \frac{C_{H^+}C_{SO_4^{2-}}}{C_{HSO_4^-}}$</td>
<td>$1.0 \times 10^{-5}$ mol cm$^{-3}$</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>$K_W = C_{OH^-}C_{H^+}$</td>
<td>$1 \times 10^{-20}$ mol$^2$ cm$^{-6}$</td>
<td>5.9</td>
<td></td>
</tr>
</tbody>
</table>

$$Cu_{total} = CuCit^- + Cu^{2+} + CuSO_4$$  \hspace{1cm} (5.10)  

$$Ni_{total} = NiCit^- + Ni^{2+} + NiSO_4$$  \hspace{1cm} (5.11)  

$$Cit_{total} = Cit^{-} + CuCit^- + NiCit^- + Na_3Cit + HCl_2^2^-$$  \hspace{1cm} (5.12)  

$$S_{total} = HSO_4^- + SO_2^{2-} + CuSO_4 + NiSO_4 + NaSO_4^- - Cu_{total} - Ni_{total}$$  \hspace{1cm} (5.13)  

$$Na_{total} = 3 \cdot Na_3Cit + Na^+ + NaSO_4^-$$  \hspace{1cm} (5.14)  

$$C_{H^+} = 10^{-pH}$$  \hspace{1cm} (5.15)  

All of the copper ions present in solution were complexed as copper citrate. The predominant nickel species was Ni$^{2+}$. The free citrate and sodium citrate concentrations were almost zero, indicating that it was completely involved in complex formation. The
Concentrations of the various species at equilibrium in the bulk are listed in Table 5.3. Concentrations below $10^{-5}$ are listed as zero, except for the $\text{OH}^-$ concentration, which is governed by the water equilibrium (Reaction 9 in Table 5.1).

**Table 5.3** Bulk concentrations of species in the electrolyte at equilibrium

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CuCit}^-$</td>
<td>0.004</td>
</tr>
<tr>
<td>$\text{CuSO}_4^-$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{NiCit}^-$</td>
<td>0.297</td>
</tr>
<tr>
<td>$\text{NiSO}_4$</td>
<td>0.714</td>
</tr>
<tr>
<td>$\text{Ni}^{2+}$</td>
<td>0.049</td>
</tr>
<tr>
<td>$\text{Cit}^3-$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Hcit}^2-$</td>
<td>0.059</td>
</tr>
<tr>
<td>$\text{Na}_3\text{Cit}$</td>
<td>0</td>
</tr>
<tr>
<td>$\text{H}^+$</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>$\text{OH}$</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>0.0785</td>
</tr>
<tr>
<td>$\text{HSO}_4^-$</td>
<td>0.00057</td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td>0.645</td>
</tr>
<tr>
<td>$\text{NaSO}_4^-$</td>
<td>0.255</td>
</tr>
</tbody>
</table>
5.1.2 Reaction Mechanisms

There are four predominant electrochemical reactions, the reduction of copper and nickel ions, the hydrogen ion reduction and the dissociation of water. During metal depositions of nickel and copper, the metal ions, $M^{n+}$ are assumed to be reduced to the solid metal, $M(s)$ in a single step, represented as

$$M^{n+} + ne^- \rightarrow M(s)$$

For simplicity, a single step deposition mechanism is considered for the copper and nickel depositions. To simulate this, all the copper reduction is assumed to be from a Cu(II) state, regardless, if it is a copper-citrate complex (CuCit⁻), or Cu²⁺ ions. An effective reaction rate ($k_{Cu(II)}$), transfer coefficient ($\alpha_{Cu(II)}$) and diffusion coefficient ($D_{Cu(II)}$) are used. Similarly, for the nickel deposition an effective reaction rate ($k_{Ni(II)}$), transfer coefficient ($\alpha_{Ni(II)}$) and diffusion co-efficient ($D_{Ni(II)}$) are used. The reduction of the metal cations at the cathode and their standard reduction potentials are shown in Table 5.4. The reduction potentials listed for the nickel and copper include both the uncomplexed metal ions as well as their citrate complexes. The following ions Na⁺, SO₄²⁻, HSO₄⁻, Cit⁻, Hcit⁻ and OH⁻ do not react electrochemically at the electrode surface.

The current densities ($i_j$) corresponding to Equations 5.16-5.19 are represented by Tafel expressions for reactant $j$.

$$i_j = -n_j F k_j C_j \exp\left(\frac{-\alpha_j n_j F E}{RT}\right)$$

$k_j$, $C_j$, $\alpha_j$, $E$ and $T$ are the rate constant, concentration (mol/cm³), transfer coefficient, overpotential (V) and temperature(K), respectively.
Table 5.4 Reduction reactions and their standard reduction potentials\textsuperscript{21,142}

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0$ vs. NHE (V)</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu(II)} + 2e^- \Leftrightarrow \text{Cu}$</td>
<td>Complexed -0.083</td>
<td>5.16</td>
</tr>
<tr>
<td></td>
<td>Uncomplexed 0.342</td>
<td></td>
</tr>
<tr>
<td>$\text{Ni(II)} + 2e^- \Leftrightarrow \text{Ni}$</td>
<td>Complexed -0.671</td>
<td>5.17</td>
</tr>
<tr>
<td></td>
<td>Uncomplexed -0.257</td>
<td></td>
</tr>
<tr>
<td>$H^+ + e^- \Leftrightarrow \frac{1}{2}H_2$</td>
<td>0.00</td>
<td>5.18</td>
</tr>
<tr>
<td>$2H_2O + 2e^- \Leftrightarrow H_2 + 2OH^-$</td>
<td>-0.828</td>
<td>5.19</td>
</tr>
</tbody>
</table>

Table 5.5 lists the values of $n_j$ and the kinetic rate expression of each reacting species. The transfer coefficients ($\alpha_j$) are listed in Table 5.6; and Table 5.7 lists the kinetic reaction constant ($k_j$) for each of the reacting species in Table 5.5. The transfer coefficient of nickel was experimentally determined from the Tafel kinetic slope and the other values of $k_j$ and $\alpha_j$ are obtained from a fit of the steady state partial current curves on a rotating cylinder electrode.

The values of the diffusion coefficients used are listed in Table 5.8. The diffusion coefficient of the Cu(II) species was determined experimentally from the copper limiting current density from the RCE experiments (Chapter 4.2.3). The other diffusion coefficients were determined from literature values\textsuperscript{21,22,141}. The diffusion coefficient used in the model for the hydrogen ion, $5 \times 10^{-4}$ cm\textsuperscript{2}/s, is larger than other reported values. The larger value thus represents the additional H\textsuperscript{+} concentration supplied from chemical equilibria and is treated as an effective diffusion coefficient. The kinematic viscosity was assumed to be the same as water, 0.01 cm\textsuperscript{2}/s. The effect of
migration and convective effects within the boundary layer are assumed negligible. The flux of all species \( (N_j) \) in this boundary layer is primarily governed by diffusion.

\[
N_j = -D_j \frac{\partial C_j}{\partial x} + R_j
\]  

(5.21)

The diffusion equation may be simplified by assuming that the homogeneous chemical equilibria of the metal-citrate species, \( R_j \), is negligible. The boundary layer thickness of the RCE is given by the Eisenberg equation (Equation 5.22) and was described in Chapter 4.2.1. The schematic of the boundary layer is shown in Figure 5.1 where the concentration of the electroactive species, \( j \), varies between the electrode surface (\( x = 0 \)) and the boundary layer thickness (\( x = \delta \)). The transport equations and boundary conditions are listed in the next section.

\[
\delta = 99.62 \ast d^{-0.4} \nu^{0.344} D^{0.356} \omega^{-0.7}
\]  

(5.22)

\[ C_j = C_j^S \quad C_j = C_j^b \]

\[ X=0 \quad X=\delta \]

**Figure 5.1** Schematic of the boundary layer and species concentrations for the RCE.
Table 5.5 Partial current density and kinetic rate expressions of the electrochemical reactions in pH 4.0 electrolyte

<table>
<thead>
<tr>
<th>Reaction</th>
<th>n</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( i_{Ni} = -2Fk_{Ni(II)}C_{Ni(II)} \exp\left(-\frac{2\alpha_{Ni(II)}FE}{RT}\right) )</td>
<td>2</td>
<td>0.16</td>
</tr>
<tr>
<td>( i_{Cu} = -2Fk_{Cu(II)}C_{Cu(II)} \exp\left(-\frac{2\alpha_{Cu(II)}FE}{RT}\right) )</td>
<td>2</td>
<td>0.18</td>
</tr>
<tr>
<td>( i_{H^+} = -Fk_{H^+}C_{H^+} \exp\left(-\frac{\alpha_{H^+}FE}{RT}\right) )</td>
<td>1</td>
<td>0.15</td>
</tr>
<tr>
<td>( i_{H_2O} = -Fk_{H_2O} \exp\left(-\frac{\alpha_{H_2O}FE}{RT}\right) )</td>
<td>1</td>
<td>0.125</td>
</tr>
</tbody>
</table>

Table 5.6 Transfer coefficients used in the kinetic expressions of Table 5.4.

<table>
<thead>
<tr>
<th>( \alpha_j )</th>
<th>Transfer coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{Cu(II)} )</td>
<td>0.18</td>
</tr>
<tr>
<td>( \alpha_{Ni(II)} )</td>
<td>0.16</td>
</tr>
<tr>
<td>( \alpha_{H_2O} )</td>
<td>0.125</td>
</tr>
<tr>
<td>( \alpha_{H^+} )</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Table 5.7 Kinetic rate constants of the partial current expressions in Table 5.5

<table>
<thead>
<tr>
<th>$k_j$</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{Cu(II)}$</td>
<td>$1.5 \times 10^{-5}$ cm.s$^{-1}$</td>
</tr>
<tr>
<td>$k_{Ni(II)}$</td>
<td>$8.75 \times 10^{-9}$ cm.s$^{-1}$</td>
</tr>
<tr>
<td>$k_{H^+}$</td>
<td>$3.5 \times 10^{-2}$ cm.s$^{-1}$</td>
</tr>
<tr>
<td>$k_{H_2O}$</td>
<td>$2.5 \times 10^{-10}$ mol.cm$^{-2}$.s$^{-1}$</td>
</tr>
</tbody>
</table>

Table 5.8 Diffusion coefficients of the electrochemical species

<table>
<thead>
<tr>
<th>$D_j$</th>
<th>Diffusion coefficient (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{Cu(II)}$</td>
<td>$1.265 \times 10^{-6}$</td>
</tr>
<tr>
<td>$D_{Ni(II)}$</td>
<td>$7.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>$D_{H^+}$</td>
<td>$5.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>$D_{OH^-}$</td>
<td>$5.5 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

5.1.3 Transport Equations and Boundary Conditions

The steady state model developed here is applied to experiments on rotating cylinder electrodes, which readily attain a steady state. Within the boundary layer
At steady state, the species of interest are the diffusing metal ions (Cu(II) and Ni(II)), hydrogen (H\(^+\)) and hydroxyl ions (OH\(^-\)). These are represented by Equations 5.27-5.29. The water equilibrium, relating the concentrations of hydrogen H\(^+\) and OH\(^-\) represented by Equation 5.30 is included and must be satisfied at all boundaries and within the diffusion layer.

\[
\begin{align*}
-D_{Ni(II)} \frac{\partial^2 C_{Ni(II)}}{\partial x^2} &= 0 \quad (5.27) \\
-D_{Cu(II)} \frac{\partial^2 C_{Cu(II)}}{\partial x^2} &= 0 \quad (5.28) \\
-D_{H^+} \frac{\partial^2 C_{H^+}}{\partial x^2} + D_{OH^-} \frac{\partial^2 C_{OH^-}}{\partial x^2} &= 0 \quad (5.29) \\
C_{H^+} C_{OH^-} - K_w &= 0 \quad (5.30)
\end{align*}
\]

At the cathode surface, \(x = 0\) the flux of the electrochemically reactive metal ions are related to their partial current by Equations 5.31 – 5.32. The side reactions of hydrogen and hydroxyl ions are included in Equations 5.33. Equation 5.30 completes the required boundary conditions at the surface of the electrode.

\[
\begin{align*}
-D_{Cu(II)} \frac{\partial C_{Cu(II)}}{\partial x} - \frac{i_{Cu}}{nF} &= 0 \quad (5.31) \\
-D_{Ni(II)} \frac{\partial C_{Ni(II)}}{\partial x} - \frac{i_{Ni}}{nF} &= 0 \quad (5.32) \\
-D_{H^+} \frac{\partial C_{H^+}}{\partial x} + D_{OH^-} \frac{\partial C_{OH^-}}{\partial x} - \frac{i_{H^+}}{F} - \frac{i_{H,0}}{F} &= 0 \quad (5.33)
\end{align*}
\]

At the boundary layer, \(x = \delta\) the ionic concentrations are equal to their bulk concentrations in solution. The bulk metal ionic concentrations are equal to their sulfate

\[126\]
concentrations in the electrolyte (Equations 5.34 - 5.35). The hydrogen ion concentration is given by the bulk pH and the hydroxyl ion bulk concentration is derived from the water equilibrium and pH (Equations 5.36 – 5.37).

\[
C_{Ni}^b - C_{Ni}^b = 0 \quad (5.34)
\]

\[
C_{Cu}^b - C_{Cu}^b = 0 \quad (5.35)
\]

\[
C_{H^+}^b - C_{H^+}^b = 0 \quad (5.36)
\]

\[
C_{OH^-}^b - C_{OH^-}^b = 0 \quad (5.37)
\]

The diffusion equations (Equations 5.27 – 5.30) and the corresponding boundary conditions (Equations 5.31 – 5.37) are solved for the concentration of each species at a given electrode potential. These one-dimensional differential equations are approximated by finite differences to a system of linear difference equations. A Runge-Kutta type algorithm, with a 3-point difference scheme was developed by J. S. Newman\textsuperscript{141} to solve second order linear, coupled differential equations. This was further refined by R.E. White\textsuperscript{140} to include 5-point difference methods. The domain is distributed into \( n \) grid points, with a spacing of \( j \), between each, providing a distance of \( nj \) between the two boundaries. The method developed by R. E. White also eliminates the use of imaginary points at the boundaries \( j = 1 \) and \( j = nj \). The number of spatial grid points employed was 100 for steady state simulations with a potential increment of 0.01 volts. The criteria for convergence was \( \frac{C_{new} - C_{old}}{C_{new}} < 10^{-4} \), where new and old are the new and old values in the iteration of the variable, \( C \).
Once the concentrations are solved, the current density of each reaction is computed as defined in Table 5.5. This is repeated for various potential steps, in increments of 0.01 V, to simulate the effects of a polarization curve on a RCE. The current efficiency is computed as

$$\eta = \frac{i_{Ni} + i_{Cu}}{i_{Ni} + i_{Cu} + i_{side}} \cdot 100$$ (5.38)

where the side reaction is defined as

$$i_{side} = i_{H^+} + i_{H_2O}$$ (5.39)

The weight percent of each metal in the alloy deposit is computed as

$$Ni(\text{wt}\%) = \frac{M_{Ni} \cdot i_{Ni}}{M_{Ni} \cdot i_{Ni} + M_{Cu} \cdot i_{Cu}} \cdot 100$$ (5.40)

$$Cu(\text{wt}\%) = \frac{M_{Cu} \cdot i_{Cu}}{M_{Ni} \cdot i_{Ni} + M_{Cu} \cdot i_{Cu}} \cdot 100$$ (5.41)

where, $M_{Ni}, M_{Cu}$ are the molecular weights of nickel and copper respectively.

### 5.2 Steady State Simulation Results

The results of steady state simulations on electrodeposition rotating cylinder electrodes are presented in this section. The two pHs used – 4.0 and 8.0 are simulated and compared with the experimental data obtained. The results of the alloy deposition and the effect of alumina on it are reported.

#### 5.2.1 Ni-Cu Alloy Simulation

##### 5.2.1.1 Low pH Simulations

The current efficiency, metal partial currents and weight percent copper are simulated for the RCE at a rotation rate of 1000 rpm. Figure 5.2 shows the simulation of the current efficiency as a function of the applied current density. For current densities,
below 10 mA/cm² the current efficiency is lower (less than 60 %). The efficiency increases to above 90 % with increasing applied current density.

Figure 5.2 Simulation of the current efficiency at pH 4.0 for a Ni-Cu electrolyte on a RCE at 1000 rpm.

Figure 5.3 shows the simulated total and metal partial current densities as functions of the applied potential. The nickel partial current is kinetically controlled in the range of experimental interest, showing an exponential increase with the potential. The copper rate approaches a limiting value at 1 mA/cm² as seen in the flat section of the simulated copper partial current curve, when the potential is more negative than -0.65 V.

The simulated effect of the weight percent copper in the deposit as a function of the applied current density is shown in Figure 5.4. The weight percent copper drops
from about 50 wt-% at low current densities to less than 5 wt-% at high current densities. At lower current densities, the nickel reaction and the copper reaction are comparable. At higher current densities, the nickel reaction increases, while the copper, which has attained its maximum limiting value remains constant. This results in the lowered copper content observed in the deposit with increasing current densities.

Figure 5.5 shows the simulation of the side reactions as functions of potential. The hydrogen ion reduction reaction exhibits a peak and a subsequent drop as the concentration of hydrogen ions at the surface of the electrode drops to zero, while the water dissociation reaction shows an exponential increase with the applied potential. The sum of the two reactions constitutes the total side reaction. The total side reaction is what is observed and calculated experimentally. The side reactions contribute to the lowering of current efficiency seen in Figure 5.2.

![Figure 5.3](image-url)

**Figure 5.3** Simulation of (a) total current density (b) Ni partial current (c) Cu partial current density at pH 4.0 for a Ni-Cu electrolyte on a RCE at 1000 rpm.
Figure 5.4 Simulation of the wt-% Cu versus the applied current density at pH 4.0 for a Ni-Cu electrolyte on a RCE at 1000 rpm.

Figure 5.5 Simulation of the partial currents of the total side reaction and at pH 4.0 for a Ni-Cu electrolyte on a RCE at 1000 rpm (a) total simulated side reaction (b) H⁺ reaction (c) H₂O reaction
5.2.1.2 High pH Simulations

For the pH 8.0 electrolyte, the simulation model is similar to the one at pH 4.0. With the addition of ammonia to the electrolyte, additional complexes and reactive species are formed. In addition to the chemical equilibria 1-9 listed in Table 5.1, copper-ammonium, nickel-ammonium and the ammonium hydroxide and water equilibrium are added, as shown by reactions 10-12 in Table 5.9. The equilibrium constants for each of them are listed in Table 5.10. Additional complexes such as Cu(NH$_3$)$_2$, Cu(NH$_3$)$_3$, Ni(NH$_3$)$_2$, Ni(NH$_3$)$_4$, Ni(NH$_3$)$_5$ are also possible, but the formation constant of Cu(NH$_3$)$_4$ and Ni(NH$_3$)$_6$ are the largest and are hence formed preferentially. These are also the electrochemically active species. The formation of metal-ammonium complex is strongly preferred over the formation of metal-citrate and other complexes, because of the high value of the equilibrium constants of these reactions$^{142-145}$. The predominant copper species in this case is Cu(NH$_3$)$_4$ and the nickel is Ni(NH$_3$)$_6$. Again, for simplicity, the copper reduction is assumed to be from a Cu(II) state, regardless, if it is a copper-citrate complex (CuCit$^-$) copper-ammonia complex (Cu(NH$_3$)$_4$) or Cu$^{2+}$. Effective values of $k_{\text{Cu(II)}}$, $\alpha_{\text{Cu(II)}}$ and $D_{\text{Cu(II)}}$ are used. Similarly, for the nickel deposition an effective reaction rate $k_{\text{Ni(II)}}$, $\alpha_{\text{Ni(II)}}$ and $D_{\text{Ni(II)}}$ are used.

Table 5.9 Chemical equilibria involving ammonia

<table>
<thead>
<tr>
<th>Reaction</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Cu^{2+} + 4NH_3 \leftrightarrow Cu(NH_3)_4$</td>
<td>10</td>
</tr>
<tr>
<td>$Ni^{2+} + 6NH_3 \leftrightarrow Ni(NH_3)_4^{2+}$</td>
<td>11</td>
</tr>
<tr>
<td>$NH_3 + H_2O \leftrightarrow NH_4OH$</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 5.10 Equilibrium constants of equilibria listed in Table 5.9

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{Cu(NH_3)<em>4^{2+}} = \frac{C</em>{Cu^{2+}} C_{NH_3}^4}{C_{Cu(NH_3)_4^{2+}}}$</td>
<td>$4.787 \times 10^{-14}$ mol$^4$ cm$^{-12}$</td>
<td>5.46</td>
</tr>
<tr>
<td>$K_{Ni(NH_3)<em>4^{2+}} = \frac{C</em>{Ni^{2+}} C_{NH_3}^6}{C_{Ni(NH_3)_4^{2+}}}$</td>
<td>$1.82 \times 10^{-9}$ mol$^6$ cm$^{-18}$</td>
<td>5.47</td>
</tr>
<tr>
<td>$K_{NH_4OH} = \frac{C_{NH_3}}{C_{NH_4^+} C_{OH^-}}$</td>
<td>$5.675 \times 10^{-10}$ mol$^{-1}$ cm$^3$</td>
<td>5.48</td>
</tr>
</tbody>
</table>

The expressions for the partial currents are governed by those listed previously in Table 5.5. The transfer coefficient ($\alpha$) of the nickel reaction was derived from experimental data, while those of the other reacting species and other constants such as, reaction rate constant ($k_j$) and the diffusion coefficients were obtained from a fit of the simulation to the data. The partition coefficients used in the simulation are listed in Table 5.11 and the reaction constants in Table 5.12. The reaction rate constants for the copper and nickel are slightly lower than the low pH electrolyte, indicating slower kinetics. The diffusion coefficients are listed in Table 5.13. The diffusion coefficients, similar to the reaction rate constants, are also lower in the case of the pH 8.0 electrolyte when compared to the pH 4.0 electrolyte. The formation of the larger ammonium complexes, slows down both the kinetics and mass transport.
Table 5.11 Transfer coefficients used in the kinetic expressions in the pH 8.0 electrolyte with ammonia

<table>
<thead>
<tr>
<th>$\alpha_j$</th>
<th>Transfer coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{Cu(II)}$</td>
<td>0.09</td>
</tr>
<tr>
<td>$\alpha_{Ni(II)}$</td>
<td>0.14</td>
</tr>
<tr>
<td>$\alpha_{H_2O}$</td>
<td>0.125</td>
</tr>
<tr>
<td>$\alpha_{H^+}$</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 5.12 Kinetic rate constants of the partial current density expressions in the pH 8.0 electrolyte with ammonia

<table>
<thead>
<tr>
<th>$k_j$</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{Cu(II)}$</td>
<td>7.5*10^{-6} cm.s^{-1}</td>
</tr>
<tr>
<td>$k_{Ni(II)}$</td>
<td>6.75*10^{-9} cm.s^{-1}</td>
</tr>
<tr>
<td>$k_{H^+}$</td>
<td>7.5*10^{-1} cm.s^{-1}</td>
</tr>
<tr>
<td>$k_{H_2O}$</td>
<td>9.5*10^{-10} mol.cm^{-2}.s^{-1}</td>
</tr>
</tbody>
</table>
Table 5.13 Diffusion coefficients of the electrochemical species used in the simulation of the pH 8.0 electrolyte with ammonia.

<table>
<thead>
<tr>
<th>$D_j$</th>
<th>Diffusion coefficient (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{Cu(ll)}$</td>
<td>$5.265 \times 10^{-7}$</td>
</tr>
<tr>
<td>$D_{Ni(ll)}$</td>
<td>$2.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>$D_{H^+}$</td>
<td>$5 \times 10^{-4}$</td>
</tr>
<tr>
<td>$D_{OH^-}$</td>
<td>$5.5 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

The partial current densities of the metal reactions are plotted both against the applied current density and the observed potential versus SCE. Figure 5.6 shows the simulated partial current densities of the copper and nickel reactions plotted against the total applied current density. Figure 5.7 is a representation of the partial current densities of nickel and copper and the total current as a function of the measured electrode potential. These are compared with the experimentally obtained data and show good agreement. A limiting current region of copper indicates mass-transport control, while the nickel is again kinetically controlled. The simulated weight percent of copper in the deposit is plotted against the applied current density in Figure 5.8. The deposit moves from a region of predominant copper (greater than 50 wt-%) at lower current densities to a region of lower copper at higher current densities. The lowering of copper in the deposit at higher current densities is because the copper rate is at its diffusional limit, while the nickel rate is still kinetically controlled and increases with applied current density.
Figure 5.9 is the simulation of the current efficiency versus the applied current density. The current efficiency increases gradually, from about 60 %, to about 80 % with increasing current density. The current efficiency is less than 100 % due to the contribution of the side reactions seen in Figure 5.10. This represents the partial current density of the side reactions versus the applied current density. The plot of the side reaction versus the observed potential is simulated and plotted in Figure 5.11. The contribution from the hydrogen side reaction is almost zero. This is due to the high value of the pH and correspondingly lower concentration of H$^+$ ions. The water dissociation side reaction is the most significant one for all applied current densities and increases exponentially with increasing potential.

![Graph](image)

**Figure 5.6** Simulation of (a) nickel and (b) copper partial current densities versus the applied current density from a pH 8.0 electrolyte with ammonia
**Figure 5.7** Simulation of (a) total current density (b) Ni and (c) Cu partial current densities versus the measured electrode potential from a pH 8.0 electrolyte with ammonia.

**Figure 5.8** Simulation of the wt-% copper in the deposit versus the applied current density from a pH 8.0 electrolyte with ammonia.
Figure 5.9 Simulation of the current efficiency versus the applied current density from a pH 8.0 electrolyte with ammonia.

Figure 5.10 Simulation of the side reaction for Ni-Cu-Al₂O₃ electrolyte at pH 8.0, with ammonia at a rotation rate of 1000 rpm.
Figure 5.11 Simulation of the side reaction versus the measured potential for Ni-Cu-Al₂O₃ electrolyte at pH 8.0 with ammonia, at a rotation rate of 1000 rpm.

5.2.2 Ni-Cu-γ Al₂O₃ Composite Simulation

5.2.2.1 Reaction Mechanism

Experimentally obtained data show that the kinetic rate of nickel deposition is not altered by the presence of alumina, but the i-E curve is shifted to more cathodic potentials. To simulate the effect of alumina nanoparticles, a surface coverage model is adopted. The alumina is assumed to cover a fraction of the surface, denoted by \( \theta \). The remainder of the surface (1-\( \theta \)) is available for electrochemical reactions to occur. The kinetic expressions of the electrochemical reactions, in Table 5.5 are modified to account for the surface coverage term, and the available area for reaction. The modified expressions are listed in Table 5.14.
Table 5.14 Partial current density and kinetic rate expressions of the electrochemical reactions in a pH 4.0 electrolyte with alumina.

<table>
<thead>
<tr>
<th>Reaction</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[ i_{\text{Ni}} = -2Fk_{\text{Ni}(II)} C_{\text{Ni}(II)} (1 - \theta) \exp\left(\frac{-2\alpha_{\text{Ni}(II)} FE}{RT}\right) ]</td>
<td>5.42</td>
</tr>
<tr>
<td>[ i_{\text{Cu}} = -2Fk_{\text{Cu}(II)} C_{\text{Cu}(II)} (1 - \theta) \exp\left(\frac{-2\alpha_{\text{Cu}(II)} FE}{RT}\right) ]</td>
<td>5.43</td>
</tr>
<tr>
<td>[ i_{\text{H}^+} = -Fk_{\text{H}^+} C_{\text{H}^+} (1 - \theta) \exp\left(\frac{-\alpha_{\text{H}^+} FE}{RT}\right) ]</td>
<td>5.44</td>
</tr>
<tr>
<td>[ i_{\text{H}<em>2\text{O}} = -Fk</em>{\text{H}<em>2\text{O}} (1 - \theta) \exp\left(\frac{-\alpha</em>{\text{H}_2\text{O}} FE}{RT}\right) ]</td>
<td>5.45</td>
</tr>
</tbody>
</table>

The kinetic parameters of nickel and copper are unaltered from the nickel-copper alloy model. The only changes to the kinetic parameters are made for the side reactions. The effect of alumina on the side reactions was experimentally confirmed to increase their rates. The higher values of \( \alpha \) and \( k \) for the side reactions reflect this increase. The parameters used for the composite simulation are listed in Table 5.15, which lists the values of \( \alpha \) and Table 5.16, which lists the values of \( k \). The diffusion coefficients are the same as the nickel-copper alloy model, with a slightly higher value of the diffusion coefficient for the hydrogen ion. The values used in this simulation are listed in Table 5.17. A high value of surface coverage (0.991) was used to simulate these results. This implies that the alumina while in contact with the electrode does not
chemically adsorb to the surface or react electrochemically. This explains the low percentage of incorporation within the deposit.

**Table 5.15** Transfer coefficients of electrochemical species in the kinetic expressions of Table 5.14.

<table>
<thead>
<tr>
<th>$\alpha_j$</th>
<th>Transfer coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{Cu(II)}$</td>
<td>0.18</td>
</tr>
<tr>
<td>$\alpha_{Ni(II)}$</td>
<td>0.16</td>
</tr>
<tr>
<td>$\alpha_{c,H_2O}$</td>
<td>0.16</td>
</tr>
<tr>
<td>$\alpha_{c,H^+}$</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**Table 5.16** Kinetic rate constants used in the expressions for partial currents in Table 5.8.

<table>
<thead>
<tr>
<th>$k_j$</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{Cu(II)}$</td>
<td>$1.5 \times 10^{-5}$ cm.s$^{-1}$</td>
</tr>
<tr>
<td>$k_{Ni(II)}$</td>
<td>$8.75 \times 10^{-9}$ cm.s$^{-1}$</td>
</tr>
<tr>
<td>$k_{H^+}$</td>
<td>$5.5 \times 10^{-2}$ cm.s$^{-1}$</td>
</tr>
<tr>
<td>$k_{H_2O}$</td>
<td>$6.0 \times 10^{-9}$ mol.cm$^{-2}$.s$^{-1}$</td>
</tr>
</tbody>
</table>
### Table 5.17 Diffusion coefficients used in the Ni-Cu-alumina simulation at pH 4.0

<table>
<thead>
<tr>
<th>$D_j$</th>
<th>Diffusion coefficient (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{\text{Cu(II)}}$</td>
<td>$1.265 \times 10^{-6}$</td>
</tr>
<tr>
<td>$D_{\text{Ni(II)}}$</td>
<td>$7.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>$D_{H^+}$</td>
<td>$7.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>$D_{\text{OH}^-}$</td>
<td>$5.5 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

#### 5.2.2.2 Ni-Cu–γ Al$_2$O$_3$ Simulation Results

Figure 5.12 shows the simulated results of the nickel and copper partial currents obtained from the surface coverage model, compared to the experimentally obtained data at pH 4.0. The cathodic shifting behavior of the nickel reaction was successfully simulated. The nickel reaction is kinetically controlled in this regime, while the copper is mass-transport controlled.

The comparison of the simulated copper –weight percent in the deposit, as a function of the applied current density, compared to that experimentally obtained, is shown in Figure 5.13. The amount of copper in the deposit decreases as the applied current increases. The simulated effect of the current efficiency and the applied current density is shown in Figure 5.14. At low current densities, the current efficiency is low, and improves to above 80 % at higher current densities. Figure 5.15 is the effect of the two side reactions and the total side reaction. The hydrogen partial current is diffusion controlled and drops to zero at higher values of the applied potential, while the water
side reaction is kinetically controlled and exhibits an exponential dependence on the applied potential. The rise of side reactions at higher currents and potentials is primarily from the water dissociation reaction.

Figure 5.16 is a comparison of the simulations of the nickel partial currents with and without alumina. The surface coverage model for alumina simulates the cathodic shift of the nickel partial current. The copper partial current is largely unaffected, except in a very small kinetic region as seen in Figure 5.17. The effect of alumina on the side reactions is to increase the net side reaction and is seen in Figure 5.18.

**Figure 5.12** Simulation of (a) total current (b) Ni and (c) Cu partial current densities at pH 4.0 for a Ni-Cu-Al₂O₃ electrolyte on a RCE at 1000 rpm
Figure 5.13 Simulation of the weight percent copper in the deposit as a function of the applied current density at pH 4.0 for a Ni-Cu-Al₂O₃ electrolyte on a RCE.

Figure 5.14 Simulation of the current efficiency versus current density for the Ni-Cu-Al₂O₃ electrolyte at pH 4.0 on a RCE at 1000 rpm.
Figure 5.15 Simulation of the side reaction for Ni-Cu-Al₂O₃ electrolyte at pH 4.0, at a rotation rate of 1000 rpm (a) total side reaction (b) H₂O reaction (c) H⁺ reaction.

Figure 5.16 Comparison of simulations of the nickel reaction with and without Al₂O₃ at pH 4.0 and a rotation rate of 1000 rpm.
Figure 5.17 Comparison of simulations of the copper reaction with and without Al₂O₃ at pH 4.0 and a rotation rate of 1000 rpm.

Figure 5.18 Comparison of simulations of the side reaction with and without Al₂O₃ at pH 4.0 and a rotation rate of 1000 rpm.
In experimentally observed data, the alumina was not significantly found to affect the rates of metal deposition. Therefore the same kinetic and mass-transport parameters obtained from nickel–copper alloy deposition from the 8.0 pH can be used, without any modifications for the composite deposition.

5.3 Non Steady State Simulation

A non-steady state model deposition for the recess was developed to understand the phenomena in deep recesses. To describe the rise in surface pH and transient currents, the buffering effect of additional species in solution and the large boundary layer have to be taken into account. In the pH 4.0 electrolyte, this is due to the bisulfate and citrate equilibrium and in the pH 8.0 electrolyte, it is the ammonium hydroxide equilibrium. The experimental depositions are carried out in the recess under a pulsed current scheme and therefore an additional constraint on the applied current has to be added to the model. The effect of different pulse on-time currents, pulse duration and buffers are simulated. The chronoamperometric experiments, described in Section 4.1.4.3 where a potential pulse is applied is also simulated.

A schematic of the recess boundary layer is shown in Figure 5.19, where the boundary layer is assumed to extend from the bottom of the recess (x = 0) to the top (x = \( \delta \)) and the concentration of species, \( j \) varies from the surface concentration, \( C^s \) to the bulk concentration, \( C^b \). Under complete diffusional polarization the surface concentration is zero. Under kinetic control, the surface concentration is the same as in the bulk and under mixed control, it is in between the bulk concentration and zero.
Figure 5.19 Schematic of the recess model

The chemical equilibrium and the equilibrium constants defined in Tables 5.1 and 5.2 for the low pH electrolyte are still valid. To take into account the chemical equilibria of bisulfate (HSO₄⁻), sulfate (SO₄²⁻), citrate (Cit³⁻), hydrogen citrate (HCit²⁻), H⁺ and OH⁻, additional transport equations are required. A time dependent term has to be accounted for in the non-steady state mass-balances for the species. In the boundary layer, \(0 < x < \delta\), the mass-balances of Cu(II), Ni(II), H⁺, OH⁻, Cit³⁻, HCit²⁻, HSO₄⁻ and SO₄²⁻ are defined by Equations 5.49 – 5.56.

5.3.1 Transport Equations and Boundary Conditions

Equations 5.49 and 5.50 are the balances for the copper and nickel species, respectively. The \(\frac{\partial}{\partial t}\) term accounts for the time dependence of the concentration. The material balance equation for H⁺, must account for the additional equilibrium reactions represented by Reactions 6 and 8, in Table 5.1. Similar mass-balances for the citrate and sulfate species are essential and are described in Equations 5.52 – 5.53. The chemical equilibrium for the citrate, bisulfate and water equilibrium are represented by Equations 5.54 – 5.56 and are valid not only for the boundary layer, but also for the surfaces. Since most of the potential drop occurs in the bulk solution, the potential gradient within the boundary layer can be considered to be zero as seen in Equation 5.57. These
9 equations now describe the non-steady state problem, with the buffering action of the citrate and bisulfate species.

\[-D_{\text{Cu(II)}} \frac{\partial^2 C_{\text{Cu(II)}}}{\partial x^2} - \frac{\partial C_{\text{Cu(II)}}}{\partial t} = 0 \]  
(5.49)

\[-D_{\text{Ni(II)}} \frac{\partial^2 C_{\text{Ni(II)}}}{\partial x^2} - \frac{\partial C_{\text{Ni(II)}}}{\partial t} = 0 \]  
(5.50)

\[-D_{H^+} \frac{\partial^2 C_{H^+}}{\partial x^2} + D_{\text{OH}^-} \frac{\partial^2 C_{\text{OH}^-}}{\partial x^2} + \frac{\partial C_{H^+}}{\partial t} - D_{\text{H}^{\text{Cu}}^-} \frac{\partial^2 C_{\text{H}^{\text{Cu}}^-}}{\partial x^2} - D_{\text{HSO}_4^-} \frac{\partial^2 C_{\text{HSO}_4^-}}{\partial x^2} = 0 \]  
(5.51)

\[-D_{\text{Cu}^{3-}} \frac{\partial^2 C_{\text{Cu}^{3-}}}{\partial x^2} - D_{\text{H}^{\text{Cu}}^-} \frac{\partial^2 C_{\text{H}^{\text{Cu}}^-}}{\partial x^2} + \frac{\partial C_{\text{Cu}^{3-}}}{\partial t} + \frac{\partial C_{\text{H}^{\text{Cu}}^-}}{\partial t} = 0 \]  
(5.52)

\[-D_{\text{SO}_4^{2-}} \frac{\partial^2 C_{\text{SO}_4^{2-}}}{\partial x^2} - D_{\text{HSO}_4^-} \frac{\partial^2 C_{\text{HSO}_4^-}}{\partial x^2} + \frac{\partial C_{\text{SO}_4^{2-}}}{\partial t} + \frac{\partial C_{\text{HSO}_4^-}}{\partial t} = 0 \]  
(5.53)

\[C_{H^+} C_{\text{HSO}_4^-} - C_{\text{HSO}_4^-} K_{\text{HSO}_4^-} = 0 \]  
(5.54)

\[C_{H^+} C_{\text{Cu}^{3-}} - C_{\text{H}^{\text{Cu}}^-} K_{\text{H}^{\text{Cu}}^-} = 0 \]  
(5.55)

\[C_{H^+} C_{\text{OH}^-} - K_W = 0 \]  
(5.56)

\[\frac{\partial \phi}{\partial x} = 0 \]  
(5.57)

At the cathode surface, \(x = 0\) the fluxes of Ni(II), Cu(II) and \(H^+\) are related to their corresponding partial current densities represented by Equations 5.58 – 5.60. The fluxes of \(\text{SO}_4^{2-}\), \(\text{HSO}_4^-\), \(\text{Cit}^3^-\), \(\text{Hcit}^2^-\) (Equations 5.61 – 5.62), and the corresponding homogeneous equilibrium Equations 5.54 – 5.56 are satisfied. For constant current depositions, the additional criteria of the sum of all partial currents being equal to the
total applied current has to be satisfied (Equation 5.63). This is not a requirement for
potentiostatic experiments.

\[-D_{Ni(II)} \frac{\partial C_{Ni(II)}^b}{\partial x} - \frac{i_{Ni}}{2F} = 0\]  
\[-D_{Cu(II)} \frac{\partial C_{Cu(II)}^b}{\partial x} - \frac{i_{Cu}}{2F} = 0\]  
\[-D_{H^{+}} \frac{\partial C_{H^{+}}}{\partial x} + D_{OH^{-}} \frac{\partial C_{OH^{-}}}{\partial x} - \frac{i_{H^{+}}}{F} - \frac{i_{H_{2}O}}{F} - D_{H_{2}^{+}} \frac{\partial C_{H_{2}^{+}}}{\partial x} - D_{HSO_{4}^{-}} \frac{\partial C_{H_{2}O_{4}^{-}}}{\partial x} = 0\]  
\[-D_{SO_{4}^{2-}} \frac{\partial C_{SO_{4}^{2-}}}{\partial x} - D_{HSO_{4}^{-}} \frac{\partial C_{HSO_{4}^{-}}}{\partial x} = 0\]  
\[-D_{Cu^{2+}} \frac{\partial C_{Cu^{2+}}}{\partial x} - D_{H_{2}Cu^{2+}} \frac{\partial C_{H_{2}Cu^{2+}}}{\partial x} = 0\]  
\[i_{Ni(II)} + i_{Cu(II)} + i_{H^{+}} + i_{H_{2}O} = i_{appl}\]  

At the boundary layer thickness, \(x=\delta\) the metal ion concentrations are equal to
their bulk concentrations and are represented by Equations 5.64 – 5.69. Equations 5.54 -
5.57 are also satisfied.

\[C_{Ni(II)}^b - C_{Ni(II)}^b = 0\]  
\[C_{Cu(II)}^b - C_{Cu(II)}^b = 0\]  
\[C_{H^{+}}^b - C_{H^{+}}^b = 0\]  
\[C_{OH^{-}}^b - C_{OH^{-}}^b = 0\]  
\[C_{Cu^{2+}} + C_{H_{2}Cu^{2+}} = C_{H_{2}Cu^{2+}}^b\]  
\[C_{SO_{4}^{2-}} + C_{HSO_{4}^{-}} = C_{HSO_{4}^{-}}^b\]
For a potentiostatic pulse or a constant potential deposition, the condition imposed by Equation 5.63, where the total current at the surface has to equal the sum of all partial currents can be relaxed. It is replaced by setting the potential equal to a constant value. The partial differential equations are approximated by the 3-point difference method for the spatial coordinates as was used for the steady state model, and a Crank-Nicholson method for time averaging. The number of spatial grid points employed was 100 and a time increment of 0.005 seconds was used.

5.3.2 Non-Steady State Simulation Results

5.3.2.1 Simulation of Surface pH Rise

Figure 5.20 shows a simulation of the surface pH rise at the bottom of the recess for different applied current densities. The initial bulk pH of the electrolyte was 4.0. Application of a current increases the potential at the electrode surface. This potential increases with higher magnitudes of applied currents (see Figure 4.1), leading to a corresponding increase in the surface pH, due to the formation of hydroxyl ions from the water reduction reaction which soon exceeds the buffering capacity of the electrolyte and results in precipitation, blocking the surface and preventing further growth, consistent with experimental observation.

The surface pH rise is both greater in magnitude and quicker in time for higher values of applied current. The figure shows a jump in the surface pH to a value greater than 10, at current density of 20 mA/cm² in about a second. At intermediate current densities (10 – 20 mA/cm²) the rise of surface pH is not as abrupt, but still increases over a period of 50 seconds. For current densities at or below 10 mA/cm², the pH value remains stable over a period of 50 seconds or longer. None of the current densities
result in a surface pH at the bulk pH of 4.0, with the lowest current density (5 mA/cm²) showing the least rise. The higher current densities result in deposits as seen in Figure 4.6.

Galvanostatic plating for long periods of time is therefore not conducive to growing tall microstructures. The effect of the surface pH rise is mitigated with decreasing boundary layer thickness or increasing deposit height. A simulation of the surface pH for different boundary layer thickness at a current density of 10 mA/cm² is shown in Figure 5.21. The rise of surface pH to a value of about 6.0 occurs at the bottom of the recess. As the thickness of the recess decreases, the surface pH value drops and remains at about its bulk value of 4.0. This implies that a shallower recess, is not subject to as high a pH rise on the application of a pulse as a deeper recess.

![Figure 5.20 Simulation of rise of surface pH with time for different applied current densities.](image)
**Figure 5.21** Simulation surface pH rise with time for an applied current density of 10 mA/cm$^2$ and different boundary layer thicknesses (a) 35 µm (b) 50 µm (c) 100 µm (d) 500 µm

### 5.3.2.2 Effect of Bulk pH and Buffer Strength

The effect of the electrolyte pH and buffering strength are expected to play a role in deep-recess plating since these are directly related to the surface pH rise and the stability of the plating process. Figure 5.22 shows the effect of a change of the electrolyte pH on the surface pH at the electrode for an applied current density of 10 mA/cm$^2$. Lowering the bulk pH results in a lowering of the surface pH. This is expected since lowering the bulk pH increases the concentration of the hydrogen ions both in the bulk and the surface, which contribute in keeping the surface pH low. The drawback of decreasing the pH is seen in Figure 5.23, which is a plot of the current efficiency at the bottom of the electrode for an applied pulse of 10 mA/cm$^2$. The current efficiency of the
pH 2.0 electrolyte is extremely low and the current efficiency of plating falls with a decrease of the electrolyte pH, which is undesirable.

Figure 5.24 is the simulated effect of increasing the buffering strength of the electrolyte, by increasing the pKa of the complexing species such as citrate or ammonium hydroxide. Increasing the buffering strength, improves the control of surface pH rise as seen. The simulated result of the increased pK value of the buffer, from 2 to 4, reduces the rise of surface pH drastically. The effect of the increased buffer strength on the current efficiency is seen in Figure 5.25, where the current efficiency drops with increase in the pK value. The drop of current efficiency however is not as dramatic as the effect of a lower pH. The current efficiency drops from over 95 % to about 70 % with the increase of pK from 2.0 to 4.0.

**Figure 5.22** Effect of different electrolyte pHs on the rise of the surface pH for an applied current density of 10 mA/cm².
Figure 5.23 Current efficiencies of electrolytes at different pHs for an applied current density of 10 mA/cm².

Figure 5.24 Effect of different buffering strengths on the rise of surface pH for an applied current density of 10 mA/cm².
Figure 5.25 Current efficiencies of different buffer strengths at a current density of 10 mA/cm².

5.3.2.3 Effect of Boundary Layer Thickness

The diffusional control of the copper species at the recess bottom is simulated in Figure 5.26, where the initial copper concentration is 0.004M. For different applied current densities, the partial current density of copper shows a drop to below 2% of its initial bulk concentration in less than 10 seconds. The drop is greater and quicker for higher applied currents. In contrast the nickel concentration plotted as a function of time is shown in Figure 5.27. The drop in surface concentration of nickel is greater for larger magnitudes of applied current, and increases with time. The drop is less than 10% of its bulk value in 10 seconds at current densities below 10 mA/cm², but increases to greater than 20% of the bulk value for larger currents at greater times. This demonstrates a
predominately kinetic control for lower currents deep within the recess, with diffusional effects influencing the reaction, particularly for larger currents.

Simulations of weight % of copper in the deposit from electrolytes with 0.004 M (pH 4.0) and 0.04 M copper (pH 8.0), as functions of time and deposit height are shown in Figures 5.28 and 5.29, respectively. The applied current density was 10 mA/cm² and the simulated results are for a 10 second on pulse. In both cases, an increased copper concentration with increasing deposit height is predicted. This agrees well with experimentally observed phenomena. The percentage of copper in the pH 4.0 electrolyte increases from about 1.5 wt-% at the bottom to about 6 wt-% at the top of the recess, while in the pH 8.0 electrolyte the copper concentration increases to about 20 wt-% at the recess mouth. These values are similar in magnitude to the actual experimental data. It is important to note a non-linear increase in copper concentration with decreasing boundary layer thickness in both cases.

![Figure 5.26](image-url)  
**Figure 5.26** Surface gradient of the copper concentration with time for different applied current densities
**Figure 5.27** Surface gradient of nickel concentration with time for different applied current densities

**Figure 5.28** Increasing wt-% Cu in the deposit with decreasing boundary layer thickness in the Ni-Cu alloy for a pH 4.0 electrolyte. (a) 500 µm (b) 250 µm (c) 50 µm (d) 350 µm (e) 25 µm
Figure 5.29 Increasing wt % Cu in the deposit with decreasing boundary layer thickness in the Ni-Cu alloy for a pH 8.0 electrolyte. (a) 500 µm (b) 250 µm (c) 50 µm (d) 30 µm (e) 25 µm (f) 20 µm (g) 10 µm

5.3.2.4 Effect of Alumina

The effect of alumina in the recess is simulated in Figure 5.30, where the surface coverage model (on a pH 4.0 electrolyte) described in Chapter 4.2.2 is simulated. The results indicate an increased concentration of the copper in the deposit for identical deposit heights in the presence of alumina. The shape of the curves is however similar to the nickel copper alloy deposition with increasing amounts of copper in the deposit with decreasing boundary layer thicknesses. The magnitude of the increase of Cu composition with alumina (about 50 %) compared to the alloy without alumina is shown in Figure 5.31. A lower boundary layer and correspondingly greater deposit height is where the effect of alumina is more pronounced. The copper concentrations in
the deposit are simulated for a boundary layer thickness of 25 µm. The increase is due to the correspondingly lowered nickel reaction rate in the presence of alumina.

In the recess, it is assumed that the presence of alumina contributes to an increase of convection, which affects the metal ion transport, and contributes, in part, to the increased copper in the deposit. Experimentally, on applying a potential step, the current transients at the bottom of the recess (see Figure 4.32) were found to increase. Convective effects can be accounted for by artificially changing the boundary layer thickness to simulate the effect of alumina in reducing the mass-transport resistance. Figure 5.32 shows the current transients obtained from a -1V pulse from a pH 4.0 electrolyte. Two different boundary layers, 250 µm and 500 µm are simulated. A high boundary layer thickness of 500 µm neglects the influence of convection, while a lowered boundary layer thickness of 250 µm can be used to describe enhancement of mass transport due to convective effects. This is attributed to the presence of alumina in the electrolyte, which helps to increase the rate of the mass-transport controlled reaction, as represented by an increase in the current.

The non-steady state model thus developed for deep recess plating provides an interpretation for the effects of various electrolyte parameters such as pH, composition and buffering strength and also plating parameters such as the applied current density, potential and time. Understanding the codeposition phenomena of alloys and composites in a recess is vital to addressing the added complexities of predicting compositional gradients, growth rates and geometry dependence.
Figure 5.30 Increasing wt % Cu in the deposit with decreasing boundary layer thickness in the Ni-Cu-γ Al₂O₃ composite deposit from a pH 4.0 electrolyte (a) 500 µm (b) 250 µm (c) 50 µm (d) 40 µm (e) 35 µm (f) 25 µm

Figure 5.31 Simulation of the weight percent of copper in the deposit from a pH 4.0 electrolyte at 10 mA/cm² and δ = 25 µm with and without alumina.
Figure 5.32 Simulation of the effect of alumina for $-1 \text{ V}$ pulse, by lowered boundary layer thickness (a) 500 $\mu$m (b) 250 $\mu$m
CHAPTER 6.

DISCUSSIONS AND CONCLUSIONS

6.1 Discussions

Experimental results indicate that alumina nanoparticles play a significant role in determining the alloy composition of nickel and copper in recessed geometries. The nanoparticles act to (i) improve the rate of diffusion limited copper in the recess and (ii) inhibit the kinetic reaction rate of Ni. The enhancement of the copper concentration in the deposits was significantly higher at greater deposit heights, irrespective of pH. In a low pH electrolyte, enhancement is observed even deep in the recess at low deposit heights. The increased deposition rate of copper may be attributed to the effect of the particles on fluid motion within the recess and its effect on surface adsorption interrupting the kinetic deposition characteristics of the metal species and side reactions.

Various forces act on the particle and influence its motion. The effects of these forces on the particle flux were enumerated by Y. Eng\textsuperscript{87} and Valdez \textit{et al.}\textsuperscript{60,150} assuming that the particles are perfect spheres and particle-particle interactions can be neglected. The equation of continuity of a particle can be written in a dimensionless form\textsuperscript{87} as

\[
\frac{\partial C_p}{\partial \tau} = D_r \frac{\partial^2 C_p}{\partial \chi^2} - K_{em} \left[ C_p \frac{\partial E}{\partial \chi} + E \frac{\partial C_p}{\partial \chi} \right] + K_{dm} \left[ C_p \frac{\partial^2 C_p}{\partial \chi^2} + \frac{\partial C_p}{\partial \chi} \frac{\partial E}{\partial \chi} \right] - D_r \frac{\partial (C_p f_{sp})}{\partial \chi} + Pe \frac{\partial C_p}{\partial \chi}
\]

(6.1)

The first term on the left results from the flux due to Brownian diffusion, the second term due to electromigration, the third term due to diffusiomigration, the fourth
term arises due to the specific forces and the fifth term is due to convection. The
dimensionless variables used are defined as follows:

\[
D_i = \frac{D_j}{D_i}; \quad C_p = \frac{c_p}{C_p}; \quad \chi = \frac{x}{a}; \quad \tau = \frac{D_j t}{a^2}; \quad E = \frac{a e E}{k T}; \quad f_{sp} = \frac{a F_{sp}}{k T}; \quad Pe = \frac{\bar{v} a}{D_j}
\]

(6.2)

where \(D_j\), \(C_p\), \(\chi\), \(\tau\), \(E\), \(f_{sp}\) and \(Pe\) are the dimensionless diffusion coefficient, particle
concentration, distance, time, electric field, specific force and Peclet number,
respectively. The diffusion coefficient of the reacting metal ion species in the
electrolyte is represented by \(D_j\) (m\(^2\) s\(^{-1}\)), \(C_p\) is the bulk concentration of particles, \(E\) the
electric field (V.m\(^{-1}\)), \(x\) the distance (m) and \(v\) the fluid velocity vector (m s\(^{-1}\)). The
coefficients \(K_{em}\) and \(K_{dm}\) are defined as

\[
K_{dm} = \frac{\varepsilon n^2 \zeta^2 C_i}{4 \pi \mu \sum_i n^2 C_i}
\]

(6.3)

and

\[
K_{em} = \frac{k T \varepsilon \zeta}{4 \pi \mu e D_j}
\]

(6.4)

where \(\varepsilon\) is the permittivity (F.m\(^{-1}\)), \(\zeta\) is the zeta potential (V), \(C_i\) is the bulk ionic
classification and \(e\) is the electronic charge (C).

Inertial forces are small in comparison to viscous forces and leads to a low
particle Reynolds number. Gravitational effects are also small due to the small mass of
the particles and therefore the gravitational term has been neglected. Due to the size of
the particles and small particle Reynolds number, Brownian motion is the significant
method of particle motion and the net transport of particles from a region of higher to
lower concentration occurs by Brownian diffusion. The diffusion coefficient of the particle, $D_p$, is determined by the Stokes-Einstein equation

$$D_p = \frac{kT}{6\pi\mu a} \tag{6.5}$$

Here, $k$ is the Boltzmann constant ($1.3807 \times 10^{-23}$ J.K$^{-1}$), $\mu$ is the solution viscosity (Ns.m$^{-2}$), $a$ is the particle radius (m) and $T$ is the absolute temperature (K). The diffusion coefficient for 32 nm alumina particles at 298 K is $1.5 \times 10^{-7}$ cm$^2$ s$^{-1}$.

The surface of oxide particles have OH- groups and other adsorbed ions. The adsorbed ions on the surface form a charged double layer and impart a net surface potential to it (zeta potential, $\zeta$). The acid base reactions on the particle surface, lead to the particle carrying a net charge. The charge depends not only on the nature of the solid oxide, but also on solution pH. In ionic solutions the particles have a positive zeta potential, if they become positively charged due to the adsorption of $H^+$, $Cu^{2+}$ and $Ni^{2+}$ or the dissociation of OH$^-$ groups. When the amount of adsorbed positive excess surface charge is equal to that of the OH$^-$ groups, the observed solution pH corresponds to the point of zero charge (pzc) of the system. Excess of adsorbed anions lead to a negative zeta potential. Both positive and negative zeta potentials have been reported based on the anions present in solution. In pH ranges below the pzc, excess cations are adsorbed on the surface, while in pH ranges above the pzc, the oxide surface has excess OH$^-$ ions or releases cations.

To codeposit on the cathode, the particle itself must attach to the cathode during the codeposition process. In the vicinity of the electrode, short range forces, result from interfacial surface effects and are termed specific forces and are represented as
\( F_{sp} = -\frac{\partial \phi_{sp}}{\partial x} \), where \( \phi_{sp} \) is the potential energy of interaction between the particle and the electrode surface. These arise from the superposition of London-Der-Waals forces, which are attractive and double layer forces, which are repulsive.

As a consequence of the double layer around the particle, effects of electrophoresis and diffusiomigration may occur. Diffusiomigration, electromigration and Brownian diffusion are schematically represented in Figure 6.1. Electrophoretic effects are due to the effect of the electric field on the particle. This effect is small due to the high conductivity and presence of a supporting electrolyte. Diffusiomigration is due to the polarization of the double layer around the particle due to the electrolyte concentration gradient. This gradient arises as the result of the depletion of metal ions at the electrode surface, leading to asymmetry in the double layer surrounding the particle. Another contribution to particle transport is a result of the physical movement of the electrolytic fluid due to natural and forced convection.

The net effect of interfacial surface effects was incorporated by Guglelmi\textsuperscript{54} and Valdes\textsuperscript{150} as a boundary condition by equating it to Butler-Volmer kinetic expression. The value of the exchange current density \( (i_0) \) depends on the composition of the solution near the electrode interface.

In order to evaluate the coefficients in equation (6.1) the typical values of the constants are assumed. For example, if \( \zeta = 10 \text{ mV}, D_e = 10^{-6} \text{ cm}^2 \text{ s}^{-1} \) at 298 K, the order of \( K_{en} \) and \( K_{dm} \) are \( 10^{-12} \) and \( 10^{-10} \), respectively. These are small compared to \( D_e \), which is 0.15 assuming a particle size of 32 nm. The fluid velocity is generally small near the electrode as the bulk convection cannot penetrate the recess depth. However due to the
motion of the particles and fluid displacement leads to a non-zero fluid velocity. The electrokinetic terms ($2^{nd}$ and $3^{rd}$) can thus be neglected compared to the $1^{st}$ and last term.

Figure 6.1 Schematic of (a) Brownian diffusion boundary layer (b) diffusiomigration and electromigration of the particle
The material balance of an ion, Equation 6.6, contains similar terms as in Equation 6.1. A non-dimensional form of the equation is presented in order to explicitly indicate the coupling of the bulk electrolytic fluid velocity $\bar{v}$, which accounts for the convective flux. The electromigration term, which is small, can be neglected in the presence of a supporting electrolyte. The resulting equation is a combination of diffusive and convective terms only,

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2} + \bar{v} \frac{\partial C_j}{\partial x}$$

(6.6)

where $D_j$ and $C_j$ are the diffusion coefficient and particle concentration of the ionic species $j$, respectively.

In the model presented in Chapter 5, the convection term is absent in Equations 5.49 and 5.50. Convection is treated as a boundary condition, establishing a mass transport boundary layer, according to a Nernst approach. Presence of the nanoparticles in the electrode can induce bulk fluid motion affecting the metal flux in Equation 6.6 or in other words decrease the boundary layer thickness used in the model presented in Chapter 5.

Local fluid motion can also be created by gas evolution, an inherent side reaction in the electrodeposition process from aqueous solutions. Vogt has studied the effect of side reactions generating hydrogen bubbles in the role of mass transport in electrochemical reactions. As a result of bubble formation, growth, and departure from the electrode surface, microconvective effects in addition to bulk macroconvective fluid flow play an important role in mass transport. D. W. Gibbons et al. have observed transport enhancements of up to 2.5 times were observed with 5-80 µm microspheres, which were attributed to the microconvective eddies produced by particle rotation in
ferricyanide reduction. These also contribute to the added convective effects of particle motion.

Convection may thus be introduced in the system either by particle motion or increased gas bubble formation in the presence of particles. This improved convection is reflected in an increase of the diffusion limited copper reaction rate in a pH 8.0 electrolyte (see Figures 4.24 and 4.25). Increasing copper concentrations in the deposit with increasing alumina concentrations in the high pH 8.0 electrolyte provide further evidence of this mechanism (Figure 4.30). At intermediate and higher deposit heights, the effect of convection due to greater particle flux is experienced, which serves to reduce the effective boundary layer and enhance the mass-transport limited reaction of copper. In a high pH electrolyte, there was no perceptible effect on the metal reaction rates in the presence of alumina as determined by RCE experiments (see Figure 4.45). In contrast, in the pH 4.0 electrolyte, the enhancement of the copper weight percent deep in the recess (see Figures 4.18 and 4.19) may be also due to the inhibition of the nickel reaction. The inhibition of the nickel rate is demonstrated by RCE data (see Figure 4.40). In addition, the rate of the side reaction was accelerated in the presence of alumina for both pHs, which results in more possible bubble formation (see Figures 4.54 and 4.57).

In low pH electrolytes, Webb et al.\textsuperscript{82} have reported a suppression of nickel reaction rate in the presence of alumina when nickel is kinetically controlled. Stojak and Talbot\textsuperscript{73} have reported both an inhibition of the copper kinetic rate and an enhancement of the Cu current density. The enhanced Cu rate occurred when the particle loading
exceeded 100 g/l, which is a different order of magnitude of particle loading than in the study presented here.

The mathematical models developed in Chapter 5, can be used to describe the deposition on flat, unrecessed electrodes and explain the process in recessed electrodes for alloys without particles. It has also been used to account for changes of the kinetic metal rate when particles are present. The influence of the particle inducing fluid motion has been artificially modeled by changing the boundary layer thickness. Thus, the model for a recessed electrode has some limits imposed by the fact that fluid dynamics and particle motion and are not explicitly solved. In addition, it does not account for the aspect ratio as it is one-dimensional. The model also does not include complete complexing equilibria and this necessitates an effective diffusion coefficient for reacting species. Therefore, to more accurately describe the change of the alloy growth and the composition profile inside the recess these features should be added. However, these themes are beyond the scope of this dissertation, which was: (1) to develop methodologies to electrodeposit alloys into recesses, and (2) study the effect of nanoparticles on the deposition rate to create, for the first time, Ni-Cu nanocomposites with microsize features.

6.2 Conclusions

The nickel copper alloy and nickel copper-alumina nanocomposite deposition was carried out on recessed electrodes and rotating cylinders from citrate electrolytes at two different pHs. Numerical models were developed to describe steady state and non-steady state deposition, which treat the metal depositions as reductions from M(II)
species to metal. The effect of alumina was simulated by a surface coverage model. The results and conclusions resulting are summarized as:

1. A graded nickel-copper alloy electrodeposited by a pulse plating scheme incorporating long off-times into 500 µm deep recesses was fabricated. Two pHs at 4.0 and 8.0 were demonstrated. This is the first such demonstration of high aspect ratio nickel-copper alloys.

2. Alumina was introduced into the electrolyte to produce a Ni-Cu-\( \gamma \) Al\(_2\)O\(_3\) nanocomposite. Electrodeposition was successfully carried out from the composite electrolyte at both pHs producing compositionally graded nanocomposites in recesses. This is the first such demonstration of a nickel copper composite either in a recess or a planar electrode.

3. The presence of alumina was found to increase the rate of copper deposition in the recess. An increase in the concentration of alumina in the electrolyte resulted in an increase in the percentage of copper in the deposit. In the low pH electrolyte, the increase was both deep in the recess and at greater heights. In the high pH electrolyte, the effect deep within the recess, was not as pronounced as in the low pH case. In both cases the enhancement of copper increased at greater heights. The morphology of the nanocomposite deposits was smoother than the alloy.

4. The enhancement of copper concentration in the microposts at the mouth or the recess corresponds to the region of highest particle concentration. In addition, greater alumina concentrations lead to an even greater enhancement.

5. The effect of alumina on the metal partial currents and the side reactions were studied using RCE experiments. In a low pH electrolyte, the alumina shifted the nickel...
reaction cathodically, while suppressing the copper reaction to a much smaller extent. No such effect was observed in the high pH electrolyte. In both electrolytes the side reaction was increased.

6. The pulsing times and duty cycles applied play an important role in deep recess plating. Long pulse off times are essential for highly recessed geometries. Increased off times beyond 70 seconds, with a 10 second on pulse did not produce any significant variation in deposit concentration, while increased on times lead to a lower concentration of copper in the deposit.

7. A steady-state mathematical model for the electrodeposition was developed to describe the alloy deposition on RCEs. The effect of alumina was incorporated by using a surface coverage model. The metal partial currents and current efficiencies were successfully simulated.

8. A non-steady-state model for the deposition in the recess was developed. The model was used to explain and understand the rise of surface pH, compositional gradients and effect of bath composition and pH on the alloy deposition in the recess.

9. The enhancement of copper in the recess in the presence of nanoparticles can be explained by considering the effects of particle motion, microconvective effects and metal rate inhibition. The effect of Brownian diffusion, diffusiomigration and microconvective eddies produced by particles contribute to the fluid motion in the recess. The effect of microconvection due to hydrogen bubble formation and inhibition of nickel rate also contributes to the enhancement of copper observed in the recess.
REFERENCES


102. Personal communication with Oscar Flores (2001).


NOMENCLATURE

\( a_{\text{ox}} \) activity of oxidized species

\( a_{\text{red}} \) activity of reduced species

\( C_j \) concentration of species \( j \), mol cm\(^{-3}\)

\( C_p \) concentration of particles, particles cm\(^{-3}\)

\( d \) cylinder electrode diameter, cm

\( d_p \) diameter of particle, cm

\( D_j \) diffusion coefficient of species \( j \), cm\(^2\) s\(^{-1}\)

\( D_p \) diffusion coefficient of particle, cm\(^2\) s\(^{-1}\)

\( e \) electronic charge, C

\( E \) potential, V

\( \mathbf{E} \) electric field, V m\(^{-1}\)

\( F \) Faraday constant, 96487 C equiv\(^{-1}\)

\( i_j \) current density of species \( j \), mA cm\(^{-2}\)

\( k \) Boltzmann constant, 1.38 \times 10^{-23} \text{ J K}^{-1}

\( k_j \) reaction rate constant of species \( j \), cm s\(^{-1}\)

\( K_W \) water dissociation constant, 1 \times 10^{-20} \text{ mol}^2 \text{ cm}^{-6}

\( K_j \) equilibrium constant of species \( j \)

\( M_j \) molecular weight of species \( j \), g mol\(^{-1}\)

\( n_j \) number of electrons transferred in the reduction of \( j \)

\( N_j \) flux of species \( j \), mol cm\(^{-2}\) s\(^{-1}\)

\( N_p \) flux of particles, particles cm\(^{-2}\) s\(^{-1}\)

\( R \) universal gas constant, 8.314 J mol\(^{-1}\) K\(^{-1}\)
\( R_s \) ohmic resistance of solution, ohm

\( t \) time, s

\( t_{on} \) pulse on time, s

\( t_{off} \) pulse off time, s

\( T \) absolute temperature, 298 K

\( x \) distance from electrode surface, cm

\( k_{rs} \) Randles-Sevcik constant, \( 2.69 \times 10^5 \text{ col mol}^{-1} \text{ V}^{-0.5} \)

\( v_{em} \) electromigration velocity, m s\(^{-1}\)

\( v_{dm} \) diffusiomigration velocity, m s\(^{-1}\)

**Indices**

\( total \) total

\( side \) side reaction

\( j \) species

\( b \) bulk

\( appl \) applied

\( dm \) diffusiomigration

\( em \) electromigration

\( p \) particle

\( ox \) oxidized

\( red \) reduced

\( rev \) reversible

\( s \) stoichiometry
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$</td>
<td>solution</td>
</tr>
<tr>
<td>$rs$</td>
<td>Randles-Sevcik</td>
</tr>
<tr>
<td>$pk$</td>
<td>peak</td>
</tr>
</tbody>
</table>

**Greek**

- $\alpha_j$: transfer coefficient of species $j$
- $\delta$: diffusion layer thickness, $\mu$m
- $\rho_p$: density of particle, g cm$^{-3}$
- $\rho_s$: density of solution, g cm$^{-3}$
- $\eta$: current efficiency, %
- $\varepsilon$: electrical permittivity, F m$^{-1}$
- $\nu$: kinematic viscosity, cm$^2$ s$^{-1}$
- $\omega$: rotation rate, rpm
- $\mu$: fluid viscosity, kg m$^{-1}$ s$^{-1}$
- $\phi$: potential, V
- $\lambda$: sweep rate, V s$^{-1}$
- $\zeta$: zeta potential, V
VITA

Amrit Panda was born in 1976 to Ramesh and Bharati Panda, in Madurai, India. He completed his high school education in New Delhi. He was accepted by Anna University in Madras, India, into the chemical engineering program and earned a Bachelor of Science degree in 1997. Later in the same year he came to the United States of America to pursue a Doctor of Philosophy degree in the Department of Chemical Engineering at Louisiana State University. He hopes to pursue a career in the emerging fields of microfabrication and nanotechnology.