Electrodeposition of FeCoNiCu quaternary system

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ELECTRODEPOSITION OF FeCoNiCu QUATERNARY SYSTEM

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

By
Qiang Huang
B.S., Zhejiang University, China, 1997
May 2004
To my parents …
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ABSTRACT

Electrodeposition is a cost-effective method to produce thin film materials, which have been used widely in the microelectronic industry, and is advantageous to fabricate metal deposits into recessed and curved areas. In this dissertation, FeCoNiCu quaternary alloy system was investigated, both experimentally and theoretically, for fabrication of multilayers, grating structures, and nanowires. Multilayer structures are composed of alternating ferromagnetic and nonmagnetic nanometric layers, and are of interest due to the giant magnetoresistance (GMR) property it possesses, a change in electric resistance in the presence of an external magnetic field. In addition, the compositional modulation, or the composition contrast, in multilayer structures can be used to develop a grating structured mold for the development of a novel nanoimprinting process.

FeCoNiCu was investigated as a more general alloy system containing iron-group metals and a nonmagnetic element, Cu, which can be simplified and adapted to any binary or ternary systems. With a dilute tartrate sulfate bath nanometric multilayers were successfully fabricated with pulse plating and GMR value was reported for this electrodeposited system for the first time. A value of -6 % was achieved on rotating disk electrode (RDE) and this maximum occurred when the structure had no preferred crystal phase. Over 40% GMR has been achieved when the multilayer was plated onto a polycrystalline Cu foil. A mathematical model was developed to tailor the deposition process on RDE, and both steady state and nonsteady state cases were simulated. A compositional gradient, which is inherent to a nonsteady state deposition process when the layer size is of nanometer scale was predicted.
The quaternary system was explored for other applications. Selective etching of electrodeposited multilayer structures was investigated for different etching solutions. A diluted K$_2$Cr$_2$O$_7$/H$_2$SO$_4$ solution was successfully developed to produce grating structures for a nanoimprinting mold, which was demonstrated with a simple cast molding process. In addition, nanowire plating was explored with different plating schemes. Nanowires of multilayers were successfully fabricated, and the nanometric layer structure was verified. A deviation was observed in the layer thickness from DC plating, as a result of the nonsteady state plating process, consistent with the model developed.
1.1 Introduction

Electrodeposition, or electroplating, is a process where an electric current is applied to produce a metal thin film by reducing cations from the electrolyte solutions. Electrodeposited alloys are used widely in the microelectronics field, due to the cost-efficiency, and the applicability to irregular geometries. It is also an advantageous method compared to other vapor techniques when depositing alloys of elements with extremely different vapor pressures.

Electroplating of iron-group metals is of much research interest due to the superior soft magnetic properties their alloys might have, which is required in data writing and reading. For example, permalloy, an alloy with 80 wt% Ni and 20 wt% Fe, was used widely in dual performance heads, because of its high saturation magnetization, low coercivity, low anisotropy field and zero magnetostriction.\(^1\) With the introduction of MR (magnetoresistivity) heads, the data reading function of the head is now performed by a MR sensor. Thus, with an increase in performance parameters, a demand for materials with improved properties, both magnetic properties and corrosion resistance, is desired for the recording head.

One approach in developing better materials is to investigate different elemental additions to alloy thin films. Cobalt is found to increase the saturation magnetization and Cu addition is a good way to both decrease the coercivity and improve the corrosion resistance.\(^1\) It was found that an electroplated zero magnetostrictive $\text{Co}_{90}\text{Fe}_{10}$ (wt%) alloy thin film has a very high saturation moment ($B_s=19$ kG) and fairly good soft magnetic properties.\(^2\) Armyanov\(^3\) studied the electrodeposited CoFe and CoNi, and correlated the magnetic properties to the
crystallographic structures. The coercivity and squareness of the hysteresis loop were found constant when the crystal structure was unchanged. The relation between composition and the magnetic properties of FeCoNi ternary alloys were extensively reviewed by Osaka.\(^4\) Favorable soft magnetic materials were prepared in a range of Co-rich chemical compositions and fine grains were found key to a low coercivity. Chang et al.\(^5\) electrodeposited CoFeCu alloys and found that the addition of Cu to CoFe results in a decreased magnetostriction and coercivity. Furthermore, the composition range over which these soft magnetic properties are obtainable is broadened.

A second approach to improve properties is to artificially structure the materials; and an easy way to do this is by layering them. When ferromagnetic materials are layered with a nonmagnetic material, such as chromium or copper, a GMR (giant magnetoresistance) effect is observed, where the resistance of the material decreases significantly when placed in a magnetic field.\(^6\) Unlayered alloy films also exhibit magnetoresistance but of a much lower value, in most cases. The GMR property is expected to have wide industrial application for data reading. One of the largest GMR materials recently published is FeCoNi/Cu fabricated with magnetron sputtering.\(^7\)\(^-\)\(^11\) A magnetoresistance up to 35% at 300 K was found\(^7\) and, a GMR effect of 16% was achieved at a very low magnetic field, 50 Oe.\(^10\)

There are different methods to fabricate multilayers, such as molecular beam epitaxy, magnetron sputtering, ion beam sputtering and vapor deposition as well as electrodeposition. All these different methods have inherent advantages and disadvantages regarding the quality of the multilayers they create and the ease of their production. Among them, electrodeposition best fulfills the imposed financial restrictions and geometrical challenges. A wide variety of
multilayer films have been electrodeposited as reviewed by Ross. However, to our knowledge, FeCoNi/Cu multilayers have not yet been fabricated by electrodeposition.

Furthermore, when the structured material fabrication is combined with the powerful capability of electrodeposition in irregular or deep recessed areas, the property of the material could be further improved. Template electroplating has been studied widely for the so-called nanowires, which refers to a wire structure having a diameter of nanometer scale. Due to its extreme shape anisotropy, nanowires allow the experimental study of some mesoscopic physics phenomenon, including a GMR measurement in a current-perpendicular-to-plane (CPP) configuration. In thin film multilayers, the layer thickness has to be comparable with the electron mean free path to exhibit GMR in a so-called current-in-plane (CIP) configuration. On the contrary, the CPP-GMR, due to the different mechanism of the MR, is governed by another characteristic length, the electron spin diffusion length, on the order of a few 10s of nm. Due to the larger characteristic length in CPP configuration, the multilayer nanowires exhibit larger GMR than the thin films.

Apart from the GMR property, a completely different possible multilayer application, taking advantage of the layered structure is for the development of a mold for grating structures. Nanoimprinting has recently been demonstrated in duplicating structures down to 10 nm from nano-molds developed from e-beam lithography. Waveguide structures with low transmission loss have been fabricated with the imprinting process, with a lithographically fabricated mold. Because of the financial restriction imposed on the lithography process, electrodeposited multilayers supplies a cost-effective competitor for grating structure mold preparation. Due to the composition contrast in the multilayered FeCoNiCu alloy, one layer could be selectively
etched by appropriate solutions, thus resulting in a grating structure for nanoimprinting process, completely avoiding the lithography step.

1.2 Goal of Study

The subject of this study is to investigate the electrodeposition of the quaternary system, Fe, Co, Ni, and Cu, for the fabrication of GMR multilayers, nanowires, and grating nanostructures. A so-called anomalous codeposition\textsuperscript{[16]} phenomenon is well known in the electrodeposition of iron group alloys. The deposition rate of Ni, the more noble element in an FeNi binary system is inhibited, when compared with its rate during elemental Ni deposition. This behavior is also observed for other binary systems of iron-group elements. Besides, the deposition rate of Fe, the less noble element, may be enhanced as recently observed\textsuperscript{[17,18]} For this quaternary system, the three iron-group elements exhibit anomalous behavior similar to the binary systems, which complicates the design and control of the plating process. In addition, because the thicknesses of the layers in the multilayer are of nanometer scale, the electrodeposition process operation may be in a non-steady state regime. Therefore, a composition profile along the deposit thickness may result\textsuperscript{[19,20]}. In order to tailor the deposit composition in a multilayer, both experimental investigation and model simulation was carried out. Despite the fact that a lot of research has been done concerning the modeling of anomalous codeposition in iron-group alloys, no studies simulate the transient behavior inherent to the GMR multilayer plating. The quaternary system of FeCoNiCu was therefore studied as a general example of iron-group alloy (FeCoNi) and nonmagnetic (Cu) elements. Our goal is to develop a time dependent model to describe the electrochemical behavior of this system that can be easily adapted to binary or ternary variations of this system.
The dissertation is composed of a study of the alloy thin films, multilayers, a model that predicts the composition gradient, a demonstration of a nanostamp and nanowire electrodeposition. In Chapter II, the FeCoNiCu quaternary system was investigated to demonstrate the anomalous electrochemical behavior. The GMR multilayers were plated and examined in Chapter III. In order to correlate the deposit composition with the plating condition, a mathematical model was developed and the simulation was performed for both steady and non-steady state cases in Chapter IV. Chapter V is about the electrodeposition of nanowires, where different plating conditions were examined with the goal of fabricating multilayer nanowires. As another application of the multilayers, selective etching was explored for the development of nano-mold for grating structures in Chapter VI.

1.3 References


CHAPTER II. INVESTIGATION OF THE ELECTROCHEMICAL SYSTEM

2.1 Introduction

2.1.1 Basic Concepts

Electrodeposition is an electrochemical reduction driven by an applied electric potential. For a reduction reaction $M^{n+} + n \, e^- \rightarrow M$, the deposition rate depends on electrolyte concentration and applied potential as governed by Equations 2-1 and 2-2.

$$-r_c = \frac{i_c}{nF} = k_c \cdot \left(C_{M^{n+}}^s\right)^{p_M}$$  \hspace{1cm} Eq.2-1

where,

$$k_c = k_{c,0} \cdot \exp\left(-\frac{\alpha_c F}{RT} \cdot E\right) = k_{c,0} \cdot \exp(-b_k \cdot E)$$  \hspace{1cm} Eq.2-2

The parameters are defined as follows: $r_c$ is the reduction rate, $i_c$ is the reduction current, $n$ is the number of electrons transferred and $F$ is the Faraday’s constant, $k_c$ is the reaction rate constant with $k_{c,0}$ being the value at zero potential, $C_{M^{n+}}^s$ is the surface concentration of the cation $M^{n+}$, $p_M$ is the reaction order of the cation, and $\frac{\alpha_c F}{RT}$, or $b_k$, is the Tafel slope, a temperature dependent variable describing the relation between reaction kinetics and potential.

The above two equations can be combined to describe the relation between current and the applied potential, as Equation 2-3. The overpotential, $\eta$, is defined as the difference between applied potential, $E$, and the equilibrium potential, $E_{rev}$, which is the potential when the total current is zero.
\[-i_s = i_0 \cdot \exp \left( -\frac{\alpha_F}{RT} \cdot \eta \right) \quad \text{Eq.2-3}\]

where the exchange current density, \( i_0 \), is a function of electrolyte concentration and the standard equilibrium potential, \( E^0 \), as described in Equations 2-4 and 2-5,

\[-i_0 = nF \cdot k_{c,0} \cdot \exp \left( -\frac{\alpha_F}{RT} \cdot \eta \right) \cdot \left( C_{M^{n+}} \right)^{\rho_m} \quad \text{Eq.2-4}\]

\[
\eta = E - E_{rev} = E - \left( E^0 + \frac{RT}{nF} \ln \left( \Pi (a_j^s)^{s_j} \right) \right) \quad \text{Eq.2-5}\]

In the Equation 2-5, the reversible potential was defined more generally, with \( a_j^s \) is the species activity at electrode surface, with the reaction stoichiometry, \( s_j \), being positive for oxidized states and negative for reduced species. The activity for solid metal is assumed to be 1 throughout this study.

As summarized in Figure 2-1, when the applied potential is low, the reduction is under kinetic control. The surface concentration of metal ions is equal to the bulk concentration, \( C^S = C^b \), and the deposition rate depends on the applied potential in an exponential manner. However when mass transport becomes important, the surface concentration is less than the bulk concentration, \( C^S < C^b \), and a gradient of ions develops at the electrode surface. As the overpotential becomes larger, the reaction rate increases and the surface concentration decreases. When the surface concentration drops to zero, the concentration gradient reaches a maximum, and the reaction rate can not increase further. This scenario describes complete transport control and the current where this occurs is called the limiting current.
The reversible potential, $E_{\text{rev}}$, is a characteristic property of the specific reaction at equilibrium conditions. The more negative $E_{\text{rev}}$, the less noble the reaction, which means the metal cation is more difficult to reduce. Table 2-1 shows the standard reversible potential ($E^0$) of the reduction of four metal elements and the possible side reactions in this study, relative to the normal hydrogen electrode (NHE). Among the four metals, Cu has a more positive $E_{\text{rev}}$, therefore it is reduced far before the others.

Accordingly, when current is passed, an alloy, rich in copper, would be produced if the concentrations and kinetic reaction rates of all metal ions are similar. In order to get around this, the Cu concentration is kept to a much lower value than the iron-group elements. By doing so, the deposition rate of Cu is controlled by mass transport, while the others are kinetically controlled. Figure 2-2 illustrates the deposition of an alloy system, when the more noble reaction is limited by mass transport. At low applied currents only copper is deposited. See point (1) in Figure 2-2. When the applied current exceeds the copper limiting current, then the alloy in
addition to copper is deposited. By elevating the current to a high value, an alloy rich in the iron-group elements is deposited with a small amount of copper. See point (2) in Figure 2-2.

**Figure 2-2.** Comparison of the deposition of iron-group elements and copper

<table>
<thead>
<tr>
<th>Electrochemical Reaction</th>
<th>Standard equilibrium Potential (V vs. NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O_2 + 4 H^+ + 4 e^- → 2 H_2O</td>
<td>1.229</td>
</tr>
<tr>
<td>Cu^{2+} + 2 e^- → Cu</td>
<td>0.3419</td>
</tr>
<tr>
<td>2 H^+ + 2 e^- → H_2</td>
<td>0</td>
</tr>
<tr>
<td>Ni^{2+} + 2 e^- → Ni</td>
<td>-0.257</td>
</tr>
<tr>
<td>Co^{2+} + 2 e^- → Co</td>
<td>-0.28</td>
</tr>
<tr>
<td>Fe^{2+} + 2 e^- → Fe</td>
<td>-0.447</td>
</tr>
<tr>
<td>2 H_2O + 2 e^- → H_2 + 2OH^-</td>
<td>-0.828</td>
</tr>
</tbody>
</table>

**2.1.2 Anomalous Codeposition**

The electrodeposition of iron-group elements has been a subject of study for a long time, due to its industrial importance as well as due to the characteristic phenomenon called anomalous codeposition. Anomalous codeposition is a term first introduced by Brenner\cite{2} to describe the
preferential reduction of the less noble metal in a binary alloy system, such as NiCo, NiFe, ZnNi and others. Among these, the NiFe system is most studied. An early investigation of this system was performed by Vagramyan and Fatueva\(^3\) in 1963. Compared with the single metal depositions, they found both a ‘retardation’ of nickel deposition and a ‘facilitation’ of iron deposition in the alloy system. As a result of this anomaly, the ratio of less noble metal (Fe) to the more noble metal (Ni) is much higher in the deposits than in the electrolyte.

Dahms and Croll\(^4\) are the first ones who put forward an explanation for anomalous codeposition, in NiFe binary system. Their model assumes that metal hydroxide and hydroxyl ions are the species that discharge at the electrode surface. Among them, the ferrous hydroxide is absorbed onto the surface before it is reduced. The hydroxide is considered stable because of the high pH calculated at the electrode surface. The inhibition of nickel reduction is due to the decrease of the available free surface resulting from the occupation of Fe(OH)\(_2\).

After this model was proposed, the effect of hydrolysis was believed to play a key role in the anomalous codeposition. Romankiw\(^5\) measured the surface pH during the electrodeposition of nickel and iron, both when deposited as single metals and as an alloy over a variety of conditions. The surface pH during deposition was found to be not high enough to lead to metal hydroxide precipitation\(^6\) and the metal monohydroxyl ion (MOH\(^+\)) was proposed to be the species discharging at the electrode surface.\(^7-9\) Hesssami and Tobias\(^7\), and Grande and Talbot\(^9\) put forward a one-dimensional diffusion model based on the discharging of the monohydroxyl ion on the electrode surface. Under this model, the concentration of the monohydroxide species at the cathode surface is directly related to the deposition of metal, and no competitive adsorption effects occur. Experimental studies with sulfate electrolytes for NiFe codeposition agreed well with their diffusional model for different bath compositions and operating conditions. Later,
Sasaki and Talbot\textsuperscript{[10]} extended the model to the other binary systems, NiCo and CoFe. Fitted equilibrium constants were needed for the metal ion and hemi-hydroxide reactions (M\textsuperscript{2+} + OH\textsuperscript{−} ⇌ MOH\textsuperscript{+}) in order for the model to simulate well the CoFe data. However, for the NiCo binary system, even fitted values compared less favorably with the experimental data. A recent paper from their group\textsuperscript{[11]} was published, modifying this model by including the blockage of hydrogen adsorption, in addition to the competitive adsorption of metal monohydroxyl intermediates. They carried out experiments with a rotating electrode and found the partial current density of iron-group deposition decreased as the rotation rate increased, and the hydrogen-blocking assumption was proposed to explain this decrease.

In 1993, a new modeling approach was proposed by Matlosz\textsuperscript{[12]}. He proposed a two-step reaction mechanism involving adsorbed monovalent intermediate ions for the electrodeposition of iron and nickel as single metals, as illustrated in Equations 2-6 and 2-7. The metal cation is reduced and adsorbed on the electrode surface, in the first step, in the form of a monovalent intermediate ion. Then the intermediate is reduced to the metal state in the second step. The model for single metal electrodeposition can be combined to form a predictive model for the codeposition of iron-nickel alloys. The preferential adsorption of the iron monovalent intermediate, resulting from the difference between the Tafel constants for the electrosorption step of the two elements, explains the apparent inhibition of Ni.

\[
M_{j}^{2+} + e^{-} \rightleftharpoons M_{j,\text{ads}}^{+} \quad \text{Eq. 2-6}
\]

\[
M_{j,\text{ads}}^{+} + e^{-} \rightleftharpoons M_{j}^{0} \quad \text{Eq. 2-7}
\]

Baker and West\textsuperscript{[13,14]} examined this model with experimental data obtained with impedance spectroscopy, and showed that the data was in agreement with the Matlosz model.
They reported an improved fit to the data by assuming the Fe reduction was 2\textsuperscript{nd} order. Krause \textit{et al.}\textsuperscript{[15]} included convection and migration with a kinetic expression that fit the experimental data. In their study, the Matlosz model was simplified under conditions of low and moderate overpotential and of low bulk Fe\textsuperscript{2+} concentration relative to that of Ni\textsuperscript{2+}. Their results showed this model fit the experimental data as well as the previous models for a narrow range of data, but lacks a physical explanation for the anomalous behavior.

While all previous models focused on the inhibition of one metal reaction rate by the other in the anomalous codeposition area, Zech \textit{et al.}\textsuperscript{[16,17]} developed a model, which described the enhancement of the less noble metal quite well by introducing a catalytic mechanism as shown in Equations 2-8 and 2-9.

\[
M_2^{++} + M_1^{++} + e^- \rightleftharpoons [M_2M_1]_{ads}^{+++} \quad \text{Eq. 2-8}
\]

\[
[M_2M_1]_{ads}^{+++} + e^- \rightleftharpoons M_2 + M_1^{++} \quad \text{Eq. 2-9}
\]

Two different iron-group metal cations in the electrolyte, a less noble metal and a more noble metal, are partially reduced and adsorbed onto the electrode surface in the form of an adsorbed mixed-metal complex. In the next step, the complex was further reduced. But instead of generating two solid metal atoms, it produces an atom of the less noble metal and, at the same time, releases a bivalent cation of the more noble metal species, acting as a catalyst. Zhuang and Podlaha\textsuperscript{[18-20]} recently showed that the anomalous behavior of the NiFeCo ternary system similarly exhibits both inhibiting and accelerating rate effects, and developed a model for the ternary system based on this mechanism.

The characteristics of the FeCoNiCu quaternary electrodeposition system have never been fully described. The three ion group elements, Fe, Co and Ni are believed to exhibit
anomalous behavior similar to the binary systems, and Cu is, in most cases, non-interactive with others, since it does not generate an adsorbed intermediate. In this chapter, an investigation is carried out for this quaternary alloy system to better characterize the electrochemical behavior, and to determine conditions for electrodepositing multilayers.

2.2. Experimental

2.2.1 Cell Design

A two-compartment cell is used in this study as illustrated in Figure 2-3. The two compartments are separate with a frit. It is designed in this manner to prevent oxidized species formed at the anode from changing the composition of the plating electrolyte at the cathode during the experiment. Both the ferrous and cobaltous ions in the electrolyte can be oxidized at the anode to the ferric and cobaltic ions.

To suppress the oxidation of ferrous and cobaltous ions by oxygen dissolved in the solution, N₂ is used to lower the concentration of dissolved oxygen. A sparger is used to introduce nitrogen into the solution. In addition, the removal of dissolved oxygen eliminates the reduction of oxidants as a possible side reaction, contributing to an increase in current efficiency. Sparging is carried out overnight before plating and is continued throughout the experiment.

A rotating disk electrode (RDE) is used as the cathode, because of its uniform boundary layer thickness and convenience in characterizing mass transport. Equation 2-10, the Levich equation, describes the relation between the boundary layer thickness and the rotation rate,

\[
\delta_N = 1.61 \cdot D_j^{1/3} \cdot \omega^{-1/2} \cdot \nu^{1/6}
\]

Eq.2-10
where $D_j$ is the diffusion coefficient of the species, $\omega$ is the angular velocity and $\nu$ is the kinematic viscosity of the solution. The material of the RDE used in this study was stainless steel. A layer of gold was plated on the RDE surface with a commercial gold solution (see Appendix A). The purpose of the gold layer was to improve the adhesion of the film to the substrate and to allow the electrochemical stripping of the deposited film. The RDE is placed in a PINE high precision rotator and the rotation rate can be controlled between 0 and 10,000 rpm.

**Figure 2-3.** Deposition cell

The disadvantage of using a RDE is that there may be edge effects, preferential plating on the edges of the disk. This occurs due to the nonuniform current distribution that develops when the reaction is influenced by the distribution of the electric field. This effect is pronounced when the reaction rate is fast, and mass transport is not dominating. Under these conditions, referred to
as primary current distribution, the current distribution is mostly determined by the electrolyte conductivity, geometry of the cell and the placement of the electrodes.

2.2.2 Electrolyte

Electrolytes used are listed below in Table 2-2. Two alloy solutions, ternary and quaternary systems, and pure metal solutions with the same metal cation concentrations have been examined. The choice of the electrolyte is based on Brownlow's work, modified here to include Co. The pH is adjusted with sulfuric acid.

Table 2-2. Composition of different solutions

<table>
<thead>
<tr>
<th></th>
<th>FeCoNiCu</th>
<th>FeNiCu</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO₄ 7H₂O (mol/L)</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoSO₄ 6H₂O (mol/L)</td>
<td>0.050</td>
<td></td>
<td></td>
<td>0.050</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiSO₄ 6H₂O (mol/L)</td>
<td>0.057</td>
<td>0.057</td>
<td></td>
<td></td>
<td>0.057</td>
<td></td>
</tr>
<tr>
<td>CuSO₄ 5H₂O (mol/L)</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td>0.001</td>
</tr>
<tr>
<td>NaKC₄H₄O₆ 4H₂O (mol/L)</td>
<td>0.027</td>
<td>0.027</td>
<td>0.027</td>
<td>0.027</td>
<td>0.027</td>
<td>0.027</td>
</tr>
<tr>
<td>Sulfamic acid (g/L)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Na Saccharin (g/L)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Triton X-100 (g/L)</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

2.2.3 Methods

The polarization curve, the steady state relationship between current and the applied potential, is determined with a PINE bipotentiostat and PineChem 2.7.5 software, which allows both potentiostat and galvanostat operations. The potentiostat was operated in the potentiostatic mode for the polarization curves, with a scan rate of 5 mV/s. A saturated calomel electrode (SCE) was used as potential reference. The potential was corrected for ohmic drop, which was measured with a Bas-Zahner IM6 impedance (details in Appendix B) measurement unit.
Current efficiency, which is the percentage of the current used in depositing the metals, was obtained with a stripping method. As mentioned above, a layer of gold was plated on top of the RDE in advance so that stripping of the deposit can be performed. Andricacos et al.\textsuperscript{[25]} has established the stripping conditions for the NiFe binary system. A chloride stripping solution was used to successfully anodize the NiFe deposit on the disk generating the Ni\textsuperscript{2+} and Fe\textsuperscript{2+} ions. The disk potential was chosen in order to dissolve the alloy without inducing any further oxidation. In their study, a rotating ring-disk electrode (RRDE) was used. When the deposit was anodically stripped from the disk potentiodynamically, the ring was kept at a constant anodic potential to oxidize Fe\textsuperscript{2+}, stripped from the disk, to Fe\textsuperscript{3+}. Later, Andricacos\textsuperscript{[26]} extended the method to the NiCo alloy, which is stripped in forms of Ni\textsuperscript{2+} and Co\textsuperscript{2+}. Horkans et al.\textsuperscript{[24]} demonstrated that the RRDE method for the composition analysis can also be used for the CuNi and CuCo alloy. A chloride electrolyte was used to strip the Cu in the form of Cu\textsuperscript{1+} and the oxidation of Cu\textsuperscript{1+} to Cu\textsuperscript{2+} was recorded on the ring at the same time.

In this study the stripping technique is used only to determine the current efficiency because there are two species that can be further oxidized by the ring. Since copper is dissolved as Cu\textsuperscript{1+}, the current efficiency can be obtained only after the composition of the deposit is known, which is analyzed with x-ray fluorescence.

A Kevex Omicron X-ray fluorescence system (XRF) was used to analyze the composition and the thickness of the alloy film. The collimator size was 100 µm, and the x-ray conditions were adjusted in an air environment to achieve a detector dead time around 50%. The composition is integrated and averaged from 20 points scanned along the diameter of each plated disk electrode. Partial current densities of different metal species were obtained from polarization, current efficiency and composition analysis.
2.3 Results and Discussion

2.3.1 Agitation Effect

Polarization curves were obtained at different agitation conditions. Figure 2-4 shows the polarization curves of the quaternary solution at different rotation rates, 500 to 4000 rpm. The ohmic drop was obtained from the impedance study, and the potential has been corrected. The effect of the rotation on the total current density was observed clearly. The limiting current densities of different reactions (plateaus in the polarization curves) increase as the agitation increases, as expected from diffusion controlled reactions. The reversible potential was unchanged. The reaction kinetics was also unchanged as the observed slope was the same for reactions at –0.2 V and –0.9 V versus SCE.

![Figure 2-4](image-url)  
**Figure 2-4.** Polarization curves of FeCoNiCu quaternary solution at the different rotation rates.

Partial current densities of different elements in the alloy solutions were calculated from the polarization, current efficiency and deposit composition, which were obtained from the stripping experiments and XRF analysis. Figure 2-5 shows partial current densities of the four
metal species in the quaternary alloy solution. As shown in Figures 2-5 (a), (b) and (c), the
deposition of Fe, Co and Ni starts at around -0.8 V versus SCE. Cu is more noble than the three
iron-group elements and starts to plate at a more positive potential of –0.2 V versus SCE. Due to
the low concentration of Cu, the limiting current was clearly observed, (Figure 2-5 (d)) which
increases with the agitation. The limiting current was not observed for the iron-group metals
except for the low rotation rate of 500 rpm.

![Graph](image)

**Figure 2-5.** Partial current densities of (a) Fe, (b) Co, (c) Ni, and (d) Cu in the FeCoNiCu
alloy solution at (+) 500, (*) 1000, (▲) 2000, and (■) 4000 rpm.
Copper limiting current densities at different agitations were obtained from Figure 2-5 (d), and plotted with different rotation rates, as shown in Figure 2-6. The limiting current density depends linearly on the square root of rotation rate, consistent with the Levich equation, Equation 2-10.

Side reaction partial current densities occurring in the FeCoNiCu electrolyte are presented in Figure 2-7. Two plateaus are observed, at around –0.5 V and –1.0 V versus SCE. Polarization curves in solutions without metal ions were performed to study the side reactions.
Figure 2-8 is the polarization at low potential with different nitrogen sparging conditions. The first part in the side reactions is confirmed to be the reduction of oxygen, since the limiting current increases as the nitrogen sparging stops and air diffuses back into solution. The limiting current density of oxygen changes from -0.08 mA/cm\(^2\) to -0.7 mA/cm\(^2\) due to an increase of oxygen content. The bulk oxygen concentration was determined from the limiting current density with a Levich\(^{[22]}\) boundary layer, as illustrated by Equation 2-11, 21 \(\mu m\) at 1000 rpm.

\[
\frac{-i_{\text{lim},O_2}}{4F} = \frac{D_{O_2} C^h_{O_2}}{\delta_{O_2}} \tag{Eq. 2-11}
\]

The diffusion coefficient from literature,\(^{[11]}\) \(D_{O_2}\), is \(2.42 \times 10^{-5}\) cm\(^2\)/s at 25 °C. The N\(_2\) sparge decreases the oxygen concentration from 5.1 ppm to as low as 0.58 ppm. This result is quite consistent with the result of Grande and Talbot in a NiFe binary system, which was measured directly with an oxygen electrode.\(^{[21]}\) Because the oxygen concentration in the solution might
vary from experiment to experiment, the effect of rotation on the limiting current in this potential range may be obscured.

**Figure 2-7.** Side reaction partial current densities in the FeCoNiCu alloy solution at (+) 500, (*) 1000, (▲) 2000, and (■) 4000 rpm.

**Figure 2-8.** Polarization at low potential at 1000 rpm, in solution with (---) N₂ sparged for overnight; (·····) N₂ sparging stopped for 30 minutes; and (——) N₂ sparging stopped for more than 3 hours.
Polarization curves at the middle potential range at different pHs are presented in Figure 2-9. The ratio of the limiting currents follows the ratio of the bulk concentration of proton, suggesting that the second part of the side reaction is due to proton reduction. The bulk concentration of proton is well defined by the pH, and the higher rotation rate increases its limiting current as predicted by the Levich Equation.

![Graph showing polarization curves at different pHs](image)

**Figure 2-9.** Polarization at mid potential at 1000 rpm, in solution with pH (— — —) 2.5, and (———) 2.0.

### 2.3.2 Solution Effect – Anomalous Codeposition

Investigations were also carried out in single metal elemental electrolytes with the same concentrations of corresponding metal species and additives. As a comparison with the quaternary alloy system, a ternary alloy solution with the same concentration of Fe, Ni and Cu was investigated as well. Figure 2-10 presents the partial current densities at 2000 rpm of the four metal elements from the ternary and quaternary alloy solutions in comparison with the single metal solutions.
Figure 2-10. Partial current densities of (a) Fe, (b) Co, (c) Ni, and (d) Cu in FeCoNiCu and FeNiCu alloy solutions in comparison with pure metal solutions, at 2000 rpm.
Anomalous codeposition\textsuperscript{[2]} behavior was observed in the alloys systems. A significant enhancement effect is observed for Fe deposition rate in the two alloy systems. The enhancement is a little greater in the quaternary system, indicating that the presence of Co enhanced the Fe plating rate, but not as significantly as Ni does. In the alloy system, a limiting current of -10 mA/cm\textsuperscript{2} at 2000 rpm was achieved at a much more positive potential than the pure Fe solution.

Co deposition rate is inhibited over most of the potential range, but a slight enhancement may occur as implied by a single data point above the crossover at about –1.1 V versus SCE. This potential corresponds to the region where Fe deposition reaches its limiting current. This concurrence is consistent with a blockage model from Fe species as the reason for Co inhibition. As the two-step mechanism proposed by Matlosz\textsuperscript{[12]} suggests, when the plating of corresponding species becomes mass transport control, the occupancy of absorbed intermediates is depleted and the inhibition of the more noble species in binary iron-group alloy systems vanishes. With the presence of Ni, a more noble iron-group metal, the effect of enhancement on Co deposition
increases as it competes with the inhibition effect from Fe, as observed in binary and ternary systems.[16-18]

The rate of Ni deposition is inhibited in alloy solutions in the potential range of study. The inhibition effects are quite similar in the two alloy solutions. The effect of Co on Ni is believed to be not as significant as the effect from Fe in the alloy system.

In spite of the above anomalous behaviors, the rates of all these three elements approach the same limiting current densities in different solutions, indicating the species’ diffusivities are same in different solutions. The presence of one metal ion doesn’t change the other metal ions considerably in terms of the diffusion, although the reaction kinetics are altered significantly at the electrode surface.

The plating of Cu, as shown in Figure 2-10(d), starts at a much more positive potential than iron-group metals, as expected, and reaches a low limiting current, -1 mA/cm², for all solutions. The scattering of data in alloy systems at the potential beyond -1.1 V versus SCE was believed due to the experimental error. The presence of iron-group metals doesn’t affect the copper plating in the limiting current range. In the kinetic region the Cu plating is inhibited in the alloy solutions, and the inhibition is more severe in the quaternary system than ternary case. This inhibition is consistent with the aforementioned mechanism for the anomalous codeposition. The adsorbed iron-group species not only inhibits the deposition of more noble iron-group metal species, but also the Cu. Thus the fractional coverage of adsorbed species must be larger in the quaternary case compared to the ternary one.

Partial current densities of side reactions are presented in Figure 2-11, for different alloy solutions and the pure Cu solution at a rotation rate of 2000 rpm. The pure Cu solution was selected for comparison because the Cu plating is believed not to involve any adsorbed species,
and even if it does, the electrode surface is yet unoccupied as the Cu plating is mass transport controlled in the potential range of interest. An inhibition is observed for the side reactions in alloy systems, taking into account that the surface of the electrode or the deposit will change the reaction kinetics. The inhibition is observed only at a potential more positive than -1.1 V, which corresponds to the potential where the Fe limiting current is reached, consistent with the aforementioned anomalous codeposition mechanism.\textsuperscript{[12]} At the very noble potential range, -0.1 to -0.6 V versus SCE, the side reaction is dominated by oxygen reduction, which also depends on the oxygen concentration as shown in Figure 2-8.

![Graph](image)

**Figure 2-11.** Partial current densities of side reactions in FeCoNiCu and FeNiCu alloy solutions in comparison with pure Cu solutions.

Figure 2-12 shows the side reaction for different pure metal solutions at 2000 rpm at a middle or high potential range. The side reaction rates are similar, except for pure Fe solutions, which is smaller than the other three. From other studies,\textsuperscript{[12-20]} the adsorbed Fe intermediate during the reduction of Fe\textsuperscript{2+} is expected to have the largest surface coverage and control the inhibition effect.
Figure 2-12. Partial current of side reactions in different pure metal solutions.

Figure 2-13 is the composition of the deposit plated at different applied currents at 2000 rpm, from FeCoNiCu and FeNiCu alloy solutions. In both solutions, pure Cu was plated at low current and alloys rich in the iron-group elements are plated when the current is high.

While the partial currents didn’t show much difference between the two alloy systems, the addition of Co exerts a big effect on the deposit composition. A maximum of Fe content was observed in both systems, which was suppressed by a high content of Co in the quaternary alloy deposit in comparison with the ternary case. Despite the fact that Co was present in the electrolyte with a concentration comparable with Ni, the Co content in the deposit is much higher, as expected for anomalous codeposition.

The effect of rotation rate on the anomalous codeposition was explored as well. Figure 2-14 shows the partial currents of the four metals in the alloy and elemental solutions at a rotation rate of 4000 rpm. The inhibition of Co and Ni and the enhancement of Fe and Co were observed, similar to the case at 2000 rpm shown in Figure 2-10.
The enhancement of Fe is more significant at a higher rotation rate. There is a switch in Co deposition rate in the alloy from predominately inhibition to enhancement occurring when the Fe deposition becomes mass transport controlled, -1 V versus SCE. Inhibition of Ni plating is observed similarly for the two alloy solutions. Copper plating is still at a limiting current, which is higher than at 2000 rpm. The scattering of data of Cu limiting current in the ternary system is due to the poor quality of the deposit, which alters the actual surface area.
Figure 2-14. Partial current of (a) Fe, (b) Co, (c) Ni, and (d) Cu in FeCoNiCu and FeNiCu alloy solutions in comparison with pure metal solutions, rotation rate is 4000 rpm.
2.4 Summary

Electrodeposition of the FeCoNiCu alloy system was investigated at different rotation rates, and compared to the pure metal solutions. The anomalous codeposition behavior of FeCoNiCu was similar to literature studies in ternary and binary iron-group alloys.

The deposition rate of Fe is enhanced and Ni is inhibited in the alloy. Both inhibition and enhancement are observed for Co. The effect on Co deposition switches from inhibition to enhancement at a potential where Fe plating reaches its limiting current. A maximum in Fe content is observed in the deposit versus the applied current, resulting from the anomalous codeposition behavior.

Comparing the quaternary alloy system to the ternary systems, the following differences were noted: i) the inhibition of the Cu deposition rate in the kinetic region was more severe in the quaternary system; ii) the maximum of the Fe content in the FeCoNiCu deposit is suppressed compared with the ternary cases, due to the high content of Co in the deposit.
The deposition of Cu is inhibited in the alloy at low potential where it is kinetically controlled, and becomes mass transport controlled at mid and high potential. The Levich equation was confirmed with an increase of limiting current of the Cu deposition and side reactions resulting from higher rotation rates.

2.5 References


3.1 Introduction

Magnetoresistance, the change of the solid state resistance due to the magnetic field environment, is one important property required for read media in computers. It is defined as the change of the resistivity with and without a magnetic field, \( \Delta \rho / \rho \). In 1988, Baibich et al.\cite{1} found that Fe/Cr superlattices exhibit giant magnetoresistance (GMR). When the various magnetic fields are applied, the resistance drops to about 50% at saturation for a Fe (30Å)/Cr(9Å) superlattice, which was deposited by molecular beam epitaxy on (001) GaAs substrates.

The antiferromagnetic (AF) coupling of the two adjacent Fe layers was attributed as the origin of GMR.\cite{2} At no external magnetic field, when two ferromagnetic Fe layers are separated by a nonmagnetic Cr layer with a proper thickness, they are antiferromagnetically coupled and have opposite electron spins. When a current passes, the current carrier, electrons, have to flip the spin direction when they pass two Fe layers, which requires extra energy, and increases the resistance. As the external magnetic field is applied and increased, the two Fe layers are forced to have same electron spins, and waives the energy required for spin-flipping, resulting in a decrease of resistance. As the AF coupling is a universal characteristic of magnetic-nonmagnetic systems, a large variety of metallic compositionally modulated multilayers were studied and GMR was characterized.\cite{3-28}

The interlayer exchange interaction, described by the RKKY (Ruderman-Kittel-Kasuya-Yosida) model\cite{29-31} and other band structure models,\cite{32-35} oscillates periodically between AF and ferromagnetic (FM) coupling as a function of the nonmagnetic layer thickness in a damped

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fashion. A schematic illustration of the oscillation is shown in Figure 3-1. Multilayers that are completely AF coupled have their GMR maximized at the first peak on a plot of GMR versus non-magnetic layer spacer thickness. Subsequent peaks correspond to lower GMR values, concomitantly having the advantage of occurring at lower saturation fields.

![Figure 3-1](image)

**Figure 3-1.** Schematic illustration of the oscillation of GMR about the thickness of nonmagnetic layer.

Most of the early GMR multilayers were prepared with physical methods, such as sputtering, molecular beam epitaxy and vapor deposition\[^{1-9}\]. Attempts to produce multilayers by electrochemical deposition have been equally promising with the added advantage of lower processing cost and the applicability to deposit onto curved and recessed substrates for nanowire designs. Preparation of electrodeposited multilayers from a single electrolyte includes a wide variety of systems, as recently reviewed\[^{10,11}\]. Those electrodeposited systems that have reported giant magnetoresistance include the following: Ni/Cu\[^{12,13}\], Co/Cu\[^{12,14-17}\], CoNi/Cu\[^{18-24}\], NiFe/Cu\[^{25-27}\] thin films and NiFe/Cu-nanowires\[^{28}\]. Among them, the electrodeposited CoNi/Cu, has been studied\[^{18-24}\] and found to exhibit maximum room-temperature GMR of over
15% in applied magnetic fields of 8 kOe. S. Z. Hua et al. found that the GMR behavior was not consistent with a damped oscillatory RKKY-type model with Cu layer spacers. They found that the second peak in the GMR with varying Cu layer thickness was larger than the first, and that the saturation field was not affected by temperature, in contrast to vapor deposited multilayers. FeNi/Cu multilayers were also electrodeposited and were found to exhibit GMR at relatively low fields. Attenborough et al. obtained 1.2% GMR at room temperature with a 5 kOe magnetic field, while a comparable value was reported by Chassaing at a lower field of 2 kOe, but also at lower temperature (77K).

In addition to GMR for which multilayers have been extensively studied, grain size might also be altered by multilayers. Grain size is nontrivial for material properties. For example, fine grains play a decisive role in acquiring a low magnetic coercivity for electrodeposited CoNiFe thin films and other alloy soft magnetic materials. Magnetoresistance in an unlayered electrodeposited cobalt alloy increased as the grains became smaller. Grain size correlation in electrodeposited multilayered structures, however, is infrequently studied. Two exceptions are the Ni/NiP and Ni/Cu multilayers studied by Ross et al. and Bonhote and Landolt, respectively. Ross et al. showed that the phosphorous content dictated the crystallite size. Bonhote and Landolt showed that the grain size was dependent upon the copper layer deposition current density. Large grains were observed when the copper layer was deposited well below the copper limiting current density, while nanosize grains were reported when the copper current density was close to its limiting value.

In this chapter, the electrodeposited quaternary Fe, Co, Ni and Cu system is explored for its multilayer potential. Co-rich FeCoNi alloys are good candidates as soft magnetic materials. Layering the Co-rich alloy with copper can increase the resistivity of the high
moment, low coercivity CoFeNi alloys, thereby avoiding eddy currents for alternatives to the traditional permalloy NiFe write material.\[43\] Furthermore, antiferromagnetic coupling can be induced with nanometric multilayers for GMR sensor applications. Jimbo et al.\[9,44-45\] have shown that NiFeCo/Cu multilayers produced by sputtering exhibit GMR in very low magnetic fields. In this chapter, we demonstrate that similar FeCoNi/Cu multilayer alloys can be easily fabricated by electrodeposition, and that the grain size can be controlled by the layer thickness. The relationship between GMR of FeCoNi/Cu multilayers and layer thickness are studied extensively at room and liquid helium temperatures. Our choice in studying this complicated quaternary system, instead of a more ideal binary system, is to develop common electrolytes and plating conditions for Ni, Co, Fe and Cu and their alloys for tailoring composition, as well as the microstructure and properties.

3.2 Experimental

3.2.1 Electrodeposition

A sulfate electrolyte containing additives was used. The constituents are listed in Table 3-1. The electrolyte is a modification of one that has been used for the electrodeposition of NiFeCu alloys by Bronlow\[54\] and Romankiw.\[55\] Here the electrolyte concentration ratios of Co/Cu and Ni/Cu are 57 and 50, respectively, due to the low Cu content in the alloy desired. The Fe electrolyte concentration is much lower than the Co and Ni because of the well-known inhibition of Ni and Co by Fe.

A two-compartment cell was used to avoid the mixing of the anodic Fe\(^{3+}\) and Co\(^{3+}\) products into the cathodic region. In order to suppress the oxidation of Fe\(^{2+}\) and Co\(^{2+}\), nitrogen was continuously sparged into the solution. A stainless steel, gold covered rotating disk electrode
(RDE) was used (diameter = 6 mm). The electrode was washed with 10% sulfuric acid and then rinsed with double distilled water, before the deposition.

Table 3-1. Bath composition for FeCoNiCu deposition

<table>
<thead>
<tr>
<th>Constituent</th>
<th>g/L</th>
<th>mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO₄·7H₂O</td>
<td>2.25</td>
<td>0.008</td>
</tr>
<tr>
<td>CoSO₄·6H₂O</td>
<td>14.0</td>
<td>0.050</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
<td>15.0</td>
<td>0.057</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
<td>0.25</td>
<td>0.001</td>
</tr>
<tr>
<td>Sodium Potassium tartrate</td>
<td>7.5</td>
<td>0.0266</td>
</tr>
<tr>
<td>Sulfamic acid</td>
<td>1.0</td>
<td>0.0103</td>
</tr>
<tr>
<td>Sodium saccharin</td>
<td>1.0</td>
<td>0.0041</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>0.6</td>
<td>0.001</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>2.5</td>
</tr>
</tbody>
</table>

Polarization curves were carried out with a Pine bi-potentiostat, and the potential was corrected for the ohmic drop, which is measured by impedance analysis with a Bas-Zahner IM6 impedance measurement unit. (Appendix B) Current efficiency was obtained by a stripping method,[56-57] using the bipotentiostat (see Chapter II). Pulse plating was performed with an Amel potentiostat together with a Waveteck function generator. The multilayer films, together with the gold bottom layer, were peeled off from the stainless steel substrate and analyzed.

Multilayers were also plated on stationary Cu foil electrode. The holder setup is detailed in Chapter V. The original thickness of Cu foil was 60 µm and was polished with sand paper and diamond paste. A layer of 50 nm Au was sputtered before electroplating.

3.2.2 Analysis

Deposit composition was analyzed with a Kevex Omicron energy dispersive X-ray fluorescence analyzer (XRF). Cross-sectional specimens for TEM observations were prepared by
cutting, mechanical grinding, polishing and dimpling followed by Ar-ion milling using a Gatan Precision Ion Polishing System (PIPS™, Model 691) at 4.5 keV at an angle of 5°. TEM studies were conducted in a JEOL JEM 2010 electron microscope operated at 200 keV with a point-to-point resolution of 2.3 Å.

X-ray powder diffraction data were obtained using a Bruker Advance D8 powder diffractometer equipped with a focusing Ge (111) incident beam monochromator (CuKα1 radiation) with a Bragg-Bretano geometry. The thin film was placed on a zero-background quartz sample holder. Intensity data were collected at ambient temperature in the 2θ range between 40° and 55° with a step width of 0.02° and an 8 s count time. The full width at half maximum (FWHM) of the peaks were determined with DIFFRACPLUS software by Bruker AXS.

The magnetoresistance (MR) effect was measured with a 9-Tesla Quantum Design PPMS measurement system using the standard 4-probe AC technique at 27 Hz with an excitation current of 1 mA. The external magnetic field was applied both parallel and perpendicular to the electric current, for the measurement of longitudinal and transverse MR, respectively.

3.3 Results and Discussion

3.3.1 Electrodeposition of Multilayers

Figures 3-2 and 3-3 show the deposit composition and current efficiency for a constant, unmodulated current density with an electrode rotation rate of 1000 rpm. At low current densities, Cu is deposited. In contrast, a Co-rich alloy is deposited at high current densities, with a small amount of copper. The anomalous behavior of the three iron group elements is also evident from Figure 3-2, similar to the cases of 2000 rpm shown in Figure 2-13. The most noble metal of the three, Ni, is present in the electrolyte with the highest concentration, but the content
of Ni in the deposit is consistently lower than Fe and Co. The current efficiency is relatively low, approaching a value of about 55% as the applied current density is increased. Both the efficiency and composition were used in the determination of the partial current densities of each reactant and to calculate the layer thickness used in the pulse plating experiments.

**Figure 3-2.** Alloy composition of the deposit DC plated at different applied current densities at 1000 rpm, o: Fe, +: Co, ▲: Ni, ■: Cu.

**Figure 3-3.** Current efficiency of the DC electrodeposition at 1000 rpm
The partial current density of each reaction is shown in Figure 3-4. The potential was determined from a polarization curve obtained at a scan rate of 5 mV/s, which was corrected for ohmic effects (see Figure 3-5). A low copper limiting current is observed, as expected. At a given potential the order of the metal deposition rate follows Co>Fe>Ni and is not consistent with the nobility order, a characteristic of anomalous codeposition.\textsuperscript{[46]}

**Figure 3-4.** Steady-state partial current densities of each element at 1000 rpm; o: Fe, +: Co, ▲: Ni, ■: Cu.

**Figure 3-5.** Polarization curve at 1000 rpm.
Based on the results above, galvanostatic pulse plating experiments were carried out between \(-3.54\) mA/cm\(^2\) for 48 seconds and \(-70.08\) mA/cm\(^2\) for 1.5 seconds. A multilayer with 10 nm Cu-rich and 20 nm Co-rich FeCoNiCu alloy was pulse plated at this condition, and the TEM micrograph is shown in Figure 3-6. The light color represents the Cu layer, and the dark one is the alloy. The thickness of each layer compares well to the calculated values based on the steady state efficiency and composition. The average molecular composition over the entire deposit is 9.5 % Fe, 47.8 % Co, 11 % Ni and 31.7 % Cu, which is consistent with the composition analysis at steady state.

![Figure 3-6](image)

**Figure 3-6.** Cross-sectional TEM micrograph of (Cu)\(_{10\text{ nm}}\) / (FeCoNiCu)\(_{20\text{ nm}}\) multilayer.

The bright field, TEM micrographs in Figure 3-7 show the grains of the multilayers with different alloy layer thickness. The grain size of the multilayer structure comprised of a 20 nm thick Cu-rich layer and a 200 nm Co-rich FeCoNiCu layer, \((\text{Cu})_{20\text{nm}}/(\text{FeCoNiCu})_{200\text{nm}}\), is on the order of 100 nm (Figure 3-7(a)). On contrast, the grains in the multilayer structure with only a 40 nm
nm Co-rich layer, (Cu)$_{20\text{ nm}}$/(FeCoNiCu)$_{40\text{ nm}}$, are of the order of 10 nm (Figure 3-7(b)). A different sample with a 20 nm Co-rich layer and a 10 nm Cu layer also confirms the grain size being on the order of 10 nm (Figure 3-7(c)). It is clearly seen that the grain size of the deposit is the same order of magnitude as the Co-rich alloy layer thickness. An electron diffraction pattern taken over a wide area of the (Cu)$_{10\text{ nm}}$/(FeCoNiCu)$_{20\text{ nm}}$ sample shows a typical nanocrystalline pattern. No grains were observed to grow across the boundaries of individual layers.

Figure 3-8 is a TEM micrograph of a bulk Co-rich FeCoNiCu alloy deposited at $-70.08$ mA/cm$^2$. The grains in the single layer structure have an average size of about 2 µm. Figures 3-8 (b)-(e) show four selected–area electron diffraction (SAED) patterns taken from the same grain. Based on the electron diffraction analysis, the electrodeposited Co-rich FeCoNiCu can be identified to have a body-centered cubic (bcc) structure with a lattice parameter of 2.9 Å. Figures 3-8(b), (c), (d) and (e) can be indexed as the [100], [110], [311] and [111] zone electron diffraction patterns of the bcc FeCoNiCu alloy.
Figures 3-6 to 3-8 indicate that the grain size can be controlled by the Co-rich alloy layer size. The bulk Co-rich FeCoNiCu alloy consists of 1000 nm (micron) size grains. In the multilayer having 20 nm Cu / 200 nm Co-rich alloy layers, the grain size is on the order of 100 nm. For the case of the 20 nm Cu / 40 nm Co-rich alloy and 10 nm Cu / 20 nm Co-rich alloy, the grains are on the order of 10 nm.
**Figure 3-8.** Alloy TEM micrograph of electrodeposited (a) Co-rich FeCoNiCu single layer structure and SAED patterns showing (b) [100], (c) [110], (d) [311] and (e) [111] zones of bcc orientation.
At a different length scale, when the calculated layer sizes are on the order of a nanometer, a preferred orientation was observed in the x-ray diffraction trace, shown in Figure 3-9. Both face-centered cubic (fcc) and bcc phases were observed. The preferred orientation depended on the thickness of the calculated Cu-rich layer when the Co-rich alloy layer was 2 nm. The three samples in Figure 3-9 were electrodeposited onto a gold plated stainless steel substrate by pulsing the current density between the Co-rich and Cu-rich alloy layer at $-35.4$ and $-0.354$ mA/cm$^2$, respectively, and then removed from the substrate. The plating time for the Co-rich alloy layer was 0.52 seconds, and the Cu-rich layers were 131, 94 and 89 seconds for each of the three deposits. The total thickness contained 730 bilayers, maintaining a constant Co-rich magnetic layer thickness. The calculated thickness of each sample was 2 nm for the Co-rich alloy and 1.7, 1.8 and 2.5 nm for the Cu-rich layers. The thicker calculated Cu multilayer deposit showed a bcc (110) preferred orientation, while an fcc (111) orientation was noted for the thinner Cu layer sample.

![XRD Analysis](image)

**Figure 3-9.** XRD analysis of three different multilayers with variable Cu-rich layer thickness, and a Co-rich layer of 2 nm. The fcc and bcc reflections are shown.
As a comparison, the XRD of copper and the electroplated Co-rich layer are shown in Figure 3-10. The fcc copper (111) and (200) peaks are present in the spectrum as well as the bcc (110) of the Co-rich alloy. The bcc phase is consistent with the electron diffraction pattern found in Figure 3-8 for the bulk alloy. Osaka\textsuperscript{[27]} has noted that both fcc and bcc phases can occur for the ternary NiCoFe system. There is a shift observed in the (111) and (110) peaks of the pure copper and alloy sample from Figure 3-10 compared to the pulsed deposits in Figure 3-9. The pulsed deposits show a shift to the right in the (111) reflection and a shift to the left for the (110) reflection, indicating in the former case a decrease in lattice parameter and in the latter an increase. Thus, the fcc peak that is shown in Figure 3-9 for the pulsed system, is due to a phase containing the iron-group elements as well as copper. The intensity ratios of the I(111)/I(200) and I(111)/I(110) for the three specimens are provided in Table 3-2. It is observed that the ratio of I(111)/I(200) increases with increasing Cu thickness, as a result of the increase intensity of the fcc copper phase. The I(111)/I(110) ratio however, decreases with increasing Cu thickness, as the bcc alloy phase dominates. If the fcc (111) reflection was exclusively due to the Cu layer

\textbf{Figure 3-10.} X-ray diffraction patterns of (a) a bulk copper and (b) Co-rich alloy layer.
thickness, with a fixed alloy bcc phase, then this ratio should increase with an increase in Cu layer thickness. Thus, the fcc (111) peak must also be indicative of an fcc alloy phase which is also consistent with the aforementioned peak shift. The FWHM for the (111), (110) and (200) reflection is fairly constant for all three samples (average value of 0.24), shown in Table 3-3, indicating that grain size (average 45 nm) is not affected by the thickness of the deposits. There is a larger crystallite size in the bcc phase compared to the fcc phase.

Table 3-2. Intensity ratios for the pulsed multilayered structures.

<table>
<thead>
<tr>
<th>Sample (Cu/Alloy)</th>
<th>I(111) / I(200)</th>
<th>I(111) / I(110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7 nm/ 2 nm</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>1.8 nm/ 2 nm</td>
<td>2.4</td>
<td>1.1</td>
</tr>
<tr>
<td>2.5 nm/ 2 nm</td>
<td>4.4</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 3-3. FWHM and calculated grain sizes.

<table>
<thead>
<tr>
<th>Sample (Cu/Alloy)</th>
<th>2θ (°) / FWHM (°) (111)</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7 nm/ 2 nm</td>
<td>43.376 / 0.24</td>
<td>35</td>
</tr>
<tr>
<td>1.8 nm/ 2 nm</td>
<td>43.389 / 0.20</td>
<td>42</td>
</tr>
<tr>
<td>2.5 nm/ 2 nm</td>
<td>43.398 / 0.22</td>
<td>40</td>
</tr>
</tbody>
</table>
### 3.3.2 Characterization of GMR Property

Figure 3-11 shows the change in resistance of the above three multilayers due to the transverse magnetic field applied at 300 K. A maximum in GMR of approximately -6 % at saturation was noted when the calculated Cu-rich layer thickness was 1.8 nm. A slightly increased or decreased Cu-rich layer yielded smaller GMR values. The largest GMR occurs when the structure shows comparable fcc and bcc peaks, *i.e.* when the $I(111)/I(110)$ ratio is closest to one, with no preferred orientation. However, these GMR values do not exceed those by Jimbo *et al.*\cite{9,44,45} for NiFeCo/Cu multilayers deposited by RF magnetron sputtering and the magnetic field required for saturation here is considerably larger. Nevertheless, this is the first demonstration of a substantial GMR in an electrodeposited CoNiFeCu/Cu alloy system.

In order to study the GMR of the electrodeposited FeCoNiCu/Cu multilayers, other multilayers were plated with various Cu layer thicknesses and a fixed Co-rich alloy layer. Figure 3-12 is the MR of a multilayer of 2.0 nm FeCoNiCu alloy and 1.4 nm Cu. Measurements of the longitudinal and transverse MR were performed at 300 K. The field required for the MR saturation is relatively high, and the transverse MR is about 2.5 % at an external field of 50 kOe.
Figure 3-11. GMR measurement in the transverse direction of multilayers with a Co-rich layer of 2 nm and Cu layer of (a) 1.7 nm, (b) 1.8 nm, and (c) 2.5 nm.
The longitude MR is lower than the transverse, but the value remains negative and the difference is small, indicating that the MR mainly results from AF coupling, and the contribution from anisotropic magnetoresistance (AMR) is relatively small, but non-zero.

![Graph](image_url)

**Figure 3-12.** Longitude (---) and transverse (—) GMR of multilayer [1.4 nm Cu / 2 nm FeCoNiCu]$_{730}$ at 300 K.

The measurement of the multilayer in Figure 3-10(b), with 1.8 nm Cu and 2.0 nm alloy, was also performed at 4 K. As seen in Figure 3-13, at 4 K the MR was significantly larger (18 %) than at room temperature, and the magnetic field required for saturation decreased to 14 kOe, consistent with the increase of mean free path of conduction electrons and the ease of AF coupling due to the low thermal randomization. In GMR thin films, the field at maximum resistance is a measure of magnetic coercivity and is temperature dependent. Figure 3-14 shows an expanded view of the GMR for both temperatures about the maximum resistance. The direction of the field sweeping is shown in the figure, and the step size is 100 Oe. At 4 K, the coercivity is about 600 Oe, and at room temperature, the coercivity is below 100 Oe, as expected for iron-group soft magnetic alloys.[36]
A series of multilayers was fabricated by changing the Cu layer deposition time. The thickness of the FeCoNiCu alloy layer was fixed at 2.0 nm, while the Cu layer thickness was varied from 1.0 to 2.5 nm. Figure 3-15 (a) shows the maximum GMR observed at 90 kOe for different Cu layer thickness. The largest value was observed at 1.8 nm. The GMR values are comparable to other electrodeposited NiCo/Cu and Co/Cu multilayers.\textsuperscript{[20-23]} This maximum GMR observed here occurs at a Cu layer thickness corresponding to the second peak in the GMR versus Cu layer thickness plot of a sputtered deposit.\textsuperscript{[9,44]} However, the first peak and the periodical oscillation behavior reported in the GMR of sputtered deposits was not observed in the electrodeposited ones, presumably due to an increase in surface roughness.

Figure 3-15 (b) shows the value of the applied magnetic field where 90% of the maximum GMR was achieved. The maximum GMR was taken at the saturation value. However, at room temperature, saturation was not always completely achieved when the instrument reached its field limit of 90 kOe. The resistance at this limit was used in determining the
Figure 3-14. GMR behavior of multilayer [1.8 nm Cu / 2 nm FeCoNiCu]$_{730}$ at low applied magnetic field at (a) 4 K and (b) 300 K.

maximum GMR value and the maximum field was equated to 90 kOe. The maximum field is much higher than comparable sputtered films at room temperature.$^{[9,44,45,58]}$ At both temperatures, as the Cu layer thickness increases, the 90% maximum field decreases with the interlayer coupling becoming weaker. The maximum GMR multilayer, which has 1.8 nm Cu layer, also shows a local maximum 90% field. This local maxima, combined with the oscillatory decreasing manner, further suggests that the observed maximum GMR corresponds to the second peak
reported for the sputtered deposited ones.\cite{2,9,44} The change in field is also depicted from Figure 3-15. Low temperature reduces the saturation field and increases GMR.

Figure 3-15. The relation between the (a) maximum transverse GMR and (b) the field where 90% of the maximum GMR is achieved with Cu layer thickness of multilayers \([x \text{ nm Cu} / 2 \text{ nm FeCoNiCu}]_{730}\) at 4 K (——) and 300 K (- - -).
Figure 3-16 presents the GMR behavior for a multilayer with a thicker alloy layer, deposited with deposition times of 94 and 0.83 seconds, corresponding to 1.8 nm Cu and 3.2 nm FeCoNiCu alloy, respectively. The saturation MR is smaller than in the sample with 2.0 nm alloy layer, but it shows significant hysteresis behavior. In granular alloys, magnetic particles dispersed in a non-magnetic matrix also exhibit a resistance dependent history, due to the possible nonuniform particle shapes and domain orientations.\textsuperscript{[2]} GMR with large nonmagnetic spacers and low interlayer coupling occurs if the magnetic layer breaks up into magnetic domains. Therefore, the thicker magnetic alloy layer electrodeposited here may be indicative of the formation of heterogeneous, anisotropic magnetic domains within the layers, accounting for the hysteresis behavior, but still retaining an appreciable antiferromagnetic coupling due to the small Cu layer thickness.

![Figure 3-16. Hysteresis GMR behavior of a multilayer [1.8 nm Cu / 3 nm FeCoNiCu]\textsuperscript{730} at 300 K, transverse direction.](image)

Figure 3-17 presents the GMR behavior for two multilayers plated on Cu foil without agitation. The current densities used in the pulse plating were -0.88 and -14.7 mA/cm\textsuperscript{2} for Cu
and Co-rich alloy, respectively. The Co-rich layer thickness was fixed by keeping the plating time constant while the Cu layer plating time varies. The current efficiency of Cu plating was assumed to be same as the value at 500 rpm RDE plating, 25%, and was assumed to be 100% at high current pulse. Therefore, the Co-rich alloy layer thickness was estimated as 2.3 nm, while the Cu layer was 1.4 nm and 1.8 nm for the two plating conditions, respectively. Compared with the multilayers plated on RDE, as shown in Figures 3-11 to 3-13, the multilayers plated on Cu foil shows significantly enhanced GMR effect, with a however larger response magnetic field, or lower sensitivity in low magnetic field. Three effects were believed to contribute the difference. Firstly, the plating was carried out without agitation, which might produce a sharper interface between layers structures (see Chapter IV). Secondly, the substrate was a polycrystalline Cu foil, instead of stainless steel. An improvement in GMR was reported for multilayers plated on polycrystalline Cu was reported by some other authors too.\[59\] Finally, the measurement was

![Figure 3-17. GMR for multilayers plated on stationary Cu foil at -14.7 mA/cm² for 0.4 seconds and -0.89 mA/cm² for (+) 16 seconds, (□) 22 seconds, with estimated layer thickness listed in the graph.](image-url)
performed with the multilayer on the Cu substrate, which contributes a short cut for current to some extent. Therefore, the magnetic field required for significant GMR effect to show up was increased.

3.4 Summary

A sulfate-tartrate electrolyte to electrodeposit FeCoNiCu quaternary alloys was developed. Cu-rich and Co-rich alloys were DC deposited at disparate current densities to produce a wide compositional range in order to produce compositionally modulated multilayered structures. The layer sizes controlled the resulting deposit grain size and preferred orientation. Changes in the Co-rich alloy layer size influenced the grain size over two orders of magnitude. Alterations in the copper layer size affected the crystallographic orientation, when the calculated layer sizes were nanometric. A combination of fcc (111) and bcc (110) iron-group phases were induced with the addition of copper. Giant magnetoresistance (-6 %) was also observed at 300 K and was correlated with fcc and bcc peak intensities that were comparable. A preferred orientation in either direction decreased the magnetoresistance.

The GMR behavior of electrodeposited FeCoNiCu/Cu multilayers was investigated with different Cu layer thickness. A single maximum in the GMR at a copper layer thickness of 1.8 nm was found, associated with a local maxima in the saturation field. Both GMR and the corresponding saturation field are temperature dependent. Hysteresis was observed in the GMR of samples having a larger magnetic layer thickness and attributed to the formation of magnetic domains within these layers. A significantly improved GMR was noted for multilayers plated on stationary Cu foil, however with an increased response magnetic field.

3.5 References


4.1 Introduction

Pulsed electrodeposition schemes of nanometric multilayers have recently been shown to exhibit GMR with numerous elemental and alloy systems, such as Co/Cu\(^{[1-5]}\), CoNi/Cu\(^{[6-9]}\), FeNi/Cu\(^{[10-12]}\) and including our own work with FeCoNiCu/Cu\(^{[13]}\) multilayers. In each of these systems the ferromagnetic layers are separated by a non-magnetic material, copper. A factor that affects GMR is the discreteness of the interface between the two different layers. In order to improve the GMR property, it is imperative to tailor and control the composition gradient within each layer. Due to the inherent characteristics of pulse plating, the deposition takes place under non-steady state conditions when the layer thickness is of nanometer scale. The transient deposition behavior is most pronounced at layer interfaces for species under diffusion control. In the fabrication of GMR multilayers, a low concentration of copper is present in the electrolyte compared to the iron-group elements. Therefore, when the magnetic layer is deposited at high current density, it is most prone to copper mass transport transient effects. A mathematical model is to be developed to describe the composition change within the magnetic alloy layer, in order to improve plating schemes for the GMR multilayer deposits.

Despite numerous experimental studies on different alloy systems and conditions in the search for better GMR, few model and simulation results have yet been reported. Yang and Cheh\(^{[14,15]}\) developed a time-dependent model with Bulter-Volmer kinetics to describe the uncoupled metal rates, with convective-diffusion mass transport. Their model was used to simulate the copper content in a magnetic, nickel layer, for Ni/Cu multilayer development, which agreed well with their experimental results. The model assumed no displacement or corrosion
reactions. Roy, et al.[16] and Bradley, et al.[17] studied the effect of corrosion during the off-time on the composition of pulse-plated Ni/Cu multilayers, in citrate and sulfamate baths, respectively. In both cases, the corrosion effect was found to be significant at short pulse off-times. Roy and Landolt[18] have developed steady-state models to describe the effect of the off-time on the displacement reaction. In their model, when the off-time is short the dissolution of Ni is controlled by the limiting cathodic current of Cu, and at long off-times it is limited by the solid state diffusion of Ni in the Cu-rich surface layer deposited as the result of displacement.

In iron-group alloy multilayers such as the FeCoNi/Cu system, the anomalous deposition behavior needs to be accounted for in order to simulate the deposit composition. Anomalous codeposition[19] refers to the preferential deposition of the less noble metal in a binary alloy system, such as NiFe, and has also been observed in ternary NiFeCo alloy mixtures.[20-22] Different mechanisms have been proposed to account for this phenomenon since the first observation of it. Dahms and Croll[23] put forward a model which assumed adsorption of metal hydroxide species resulting in the inhibition of the more noble metal. Subsequent models adopted the monohydroxyl ion as the species discharging at the electrode surface since the pH required for the formation of hydroxyl precipitation might be prohibitively high.[24] A series of systematic studies based on this mechanism were performed by Talbot et al.[25-28] Another approach proposed by Matlosz[29] involved the generation and competitive adsorption of monovalent intermediates. Recently, Zech et al.[30] introduced a catalytic mechanism into the model to account for not only the inhibition of the more noble species, but also the enhancement of the less noble metal deposition. Zhuang and Podlaha[22,31,32] studied the anomalous behavior of FeCoNi alloy system extensively, and observed both the inhibition and the enhancement in the ternary system. They combined the mechanism by Matlosz and Zech et al. and developed a model for the ternary system.
In this chapter, a time dependent model is presented which merges the anomalous mechanistic model with mass transport to describe compositional gradients at the start of each magnetic layer interface in nanometric multilayer development. Due to the anomalous behavior of iron-group elements, the deposition composition becomes less straightforward when the transient effect is considered. The adsorbed species accumulate as deposition progresses, and the competitive interaction deviates from the steady state case. Simultaneously, before steady state is achieved, the deposition rate of Cu changes as its surface concentration depletes with time.

4.2 Model Development

The following assumptions are included in the model:

1. Dilute solution theory holds.

2. Temperature is constant.

3. Double layer charging/discharging is negligible.

4. Proton cation and hydroxyl anion are in equilibrium with water.

5. Concentration and potential variations in the radial direction are neglected.

6. Effect of nucleation is neglected during deposition, which is assumed to be uniform across the surface.

7. Langmuir adsorption is assumed and only a single layer of adsorbed species is allowed at the electrode surface.

As a consequence of the presence of supporting electrolyte, migration is small and neglected in the model. Therefore, the mass transport in the electrolyte consists of diffusion and convection only, and the mass balance thus is governed by
\[
\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x^2} - u_x \frac{\partial C_j}{\partial x}
\]
Eq. 4-1

where \( D_j \) is the diffusion coefficient of the species \( j \), \( x \) and \( u_x \) are the axial coordinate from the RDE surface and the axial velocity, respectively. Near the RDE, \( u_x \) is analytically derived as

\[
u \omega \frac{\partial^2 C_j}{\partial x^2} \sim \frac{1}{2} \frac{\partial C_j}{\partial x} + \frac{1}{2} x^2
\]
Eq. 4-2

where \( \omega \) is the angular velocity and \( \nu \) is the kinematic viscosity of the solution.

The initial and boundary conditions for Equation 4-1 are:

at \( t = 0, x \geq 0 \) \( C_j = C_j^b \) Eq. 4-3

\[
\sum s_{jk} r_k = 0
\]
Eq. 4-5

where \( C_j^b \) is the bulk concentration of species \( j \), \( s_{jk} \) is the stoichiometric number of species \( j \) in reaction \( k \), and \( r_k \) is the rate of reaction \( k \). In the numerical simulation, the end boundary was set as 150 \( \mu \)m, much larger than the boundary layer thickness estimated from Levich’s Equation,\(^{[32]}\) for each reacting species. The boundary layer for each species was calculated according to Levich, Equation 2-10.

Anomalous codeposition behavior of the iron-group metals (Fe, Co, Ni) is simulated with a two-step mechanism involving monovalent intermediates and a catalytic mechanism.\(^{[29,30]}\) The anodic and cathodic reaction components follow Tafel kinetics, according to Equations 2-1 and 2-2.
Step 1 \[ M_j^{++} + e^- \rightleftharpoons M_{j,ads}^+ \] Eq. 4-6

\[ r_k = k_k \cdot C_{M_j^{++}} \cdot \theta_{empty} - k_{-k} \cdot \theta_{M_j^{++},ads} \] Eq. 4-7

Step 2 \[ M_{j,ads}^+ + e^- \rightleftharpoons M_j^+ \] Eq. 4-8

\[ r_k = k_k \cdot \theta_{M_{j,ads}} - k_{-k} \cdot a_{M_j} \] Eq. 4-9

Catalytic step 1 \[ M_2^{++} + M_1^{++} + e^- \rightleftharpoons [M_2M_1]_{ads}^{+++} \] Eq. 4-10

\[ r_k = k_k \cdot C_{M_2^{++}} \cdot C_{M_1^{++}} \cdot \theta_{empty} - k_{-k} \cdot \theta_{[M_2M_1]_{ads}^{+++}} \] Eq. 4-11

Catalytic step 2 \[ [M_2M_1]_{ads}^{+++} + e^- \rightleftharpoons M_2 + M_1^{++} \] Eq. 4-12

\[ r_k = k_k \cdot \theta_{[M_2M_1]_{ads}^{+++}} - k_{-k} \cdot C_{M_1^{++}} \cdot a_{M_2} \cdot \theta_{empty} \] Eq. 4-13

where \( M \) represents metal species. The designation of subscripts 1 and 2, \( M_1 \) and \( M_2 \), indicate the more (1) and less (2) noble elements, respectively in any paired combination of Co, Ni and Fe.

The fractional surface coverage, \( \theta \), is either empty or occupied by species. The activity of solid metal, \( M_j \), is designated as \( a_{M_j} \), and assumed to be one. The cathodic and anodic reaction rate constants are designated as \( k_k \) and \( k_{-k} \) respectively.

The catalytic mechanism in equations 4-10 to 4-13 is applied only to the less noble species of the three possible binary combinations, NiFe, NiCo, and CoFe. Therefore, for the ternary iron-group mixture, six equations are needed, each with independent kinetic constants. In addition, equations 4-6 to 4-9 represent 6 additional equations for Fe, Co, and Ni.
The reduction of copper ions is treated as a single step elemental reaction, neglecting the anodic reaction, and the kinetics follow the same reaction form as equation 4-7, without the last term on the right hand side.

\[
\text{Cu(II)} + 2 \text{e}^- \rightarrow \text{Cu} \quad \text{Eq. 4-14}
\]

Reduction of copper has been extensively studied. Chassaing et al.\textsuperscript{[35]} showed that complexed species govern Cu kinetic rates in citrate electrolytes. A recent study\textsuperscript{[36]} was performed on the deposition mechanism for the copper tartrate system at high pH. The copper cation was complexed with tartrate and the reduction mechanism occurred via two consecutive steps, with a non-adsorptive monovalent cation intermediate.

Reduction of proton is simulated with a two-step Volmer-Tafel mechanism, involving neutral adsorbed intermediates. In the second step, the adsorbed species combine with each other to form hydrogen, independent of potential. Similar to metal ions, protons can also be in a complex form.

\[
\text{H(1)} + \text{e}^- \rightarrow \text{H}_{\text{ads}} \quad \text{Eq. 4-15}
\]

\[
r_k = k_k \cdot C_{H(1)} \cdot \theta_{\text{empty}} \quad \text{Eq. 4-16}
\]

\[
\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2 \quad \text{Eq. 4-17}
\]

\[
r_k = k_k \cdot \theta_{H_{\text{ads}}}^2 \quad \text{Eq. 4-18}
\]

where kinetic constants are designated in the same way as in equations 4-6 to 4-9, and the anodic parts of the reaction are neglected.
In this work, the complexing equilibrium is neglected. Equilibrium calculations based on literature stability constants\cite{37} show that, at a bulk pH of 2.5, most of the tartrate anions are complexed with Co\(^{2+}\) and H\(^+\), and all the metal ions are present in the solution as free cations. (See Appendix C for detailed equations). The diffusion coefficients and kinetic constants were determined from a steady state analysis, and these values, therefore represent an average contribution from reacting species that are both complexed and uncomplexed.

Reduction of oxygen and the dissociation of water are both accounted for with a simplified one-step reaction. And the anodic parts of the two reactions are assumed to be small and negligible.

\[
\begin{align*}
\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- & \longrightarrow 2 \text{H}_2\text{O} \quad \text{Eq. 4-19} \\
\theta & = k \cdot C\text{O}_2 \cdot C\text{H}^+ \cdot \theta_{\text{empty}} \quad \text{Eq. 4-20} \\
2\text{H}_2\text{O} + 2\text{e}^- & \longrightarrow 2\text{OH}^- + \text{H}_2 \quad \text{Eq. 4-21} \\
\theta & = k \cdot \theta_{\text{empty}} \quad \text{Eq. 4-22}
\end{align*}
\]

For those reduction mechanisms with adsorbed intermediates involved, the difference of the rates of the two consecutive steps results in the change of surface coverage of the associated intermediate.

\[
\frac{\partial \theta_j}{\partial t} = -A \cdot (r_{j,1} - r_{j,2}) \quad \text{Eq. 4-23}
\]

where \( A \) is the surface area occupied by a unit amount of adsorbed intermediates, calculated as \((2.5 \times 10^{16})N_{\text{Avogadro}} \text{ cm}^2/\text{mol}\), and the \( r_{j,1} \) and \( r_{j,2} \) are the reaction rates of the two steps.
generating and consuming the intermediates, respectively. The sum of occupied fraction of all species and the empty fraction should be unity.

\[ \theta_{empty} = 1 - \sum_j \theta_j \]  

Eq. 4-24

At galvanostatic conditions, the total current is constant.

\[ - \sum_k n_k F \cdot r_k = i_{total} \]  

Eq. 4-26

With the reaction mechanism 4-6 to 4-25, the mass balance equations in 4-1 to 4-5 were solved simultaneously to determine the concentration profile for all species in the electrolyte and surface coverage occupied by different adsorbed intermediates. The differential equations were cast in a three-point finite difference form following the Crank-Nicholson method and linearized numerically as outlined by Bennion.\[45\] The system of ordinary, differential equations were then solved by a Newton-Raphson method adapted from Newman’s BAND(J) subroutine.\[46\] In the steady state case, the left side of Equation 4-1 becomes zero, the mass balance becomes time independent, and the simulation is simplified.

After the concentration profile, adsorption coverage and the potential were obtained, reaction rates or partial current densities were calculated. The thickness, \( d \), and composition of the deposit, \( x_j \), can be determined from the partial currents of different species as follows.

\[
d = \sum_{\Delta t} \sum_j \left( \frac{MW_j}{\rho_j} \sum_k \left( - s_{jk} r_k \cdot \Delta t \right) \right) \]  

Eq. 4-27

\[
x_j = \frac{\sum_{\Delta t} \left( MW_j \sum_k \left( - s_{jk} r_k \cdot \Delta t \right) \right)}{\sum_{\Delta t} \sum_j \left( MW_j \sum_k \left( - s_{jk} r_k \cdot \Delta t \right) \right)} \]  

Eq. 4-28
where $MW_j$ and $\rho_j$ are the molecular weight and density of metal $j$, respectively, and $\Delta t$ is the step of time increment for calculation.

The model does not take into account non-uniform nucleation nor the formation of different phases. For example, Co and Cu are known to be thermodynamically immiscible,\cite{47} and columnar Co-rich phases are known to occur surrounded by discrete Cu-rich phases.\cite{48} The presence of saccharin has been shown to improve the homogeneity of the CoCu\cite{48} and CuNi\cite{49} phases and has been used in the experimental part of this study. Thus, the model presented here is more suitable for uniform microstructures.

### 4.3 Experimental

The experimental setup was described previously in Chapter II. The quaternary alloy sulfate electrolyte with additives was used. Metal ion concentrations were, 8 mM FeSO$_4$, 50 mM CoSO$_4$, 57 mM NiSO$_4$, and 1 mM CuSO$_4$. Sodium potassium tartrate (27 mM), sulfamic acid (10 mM), sodium saccharin (4 mM) and triton X-100 (0.6 g/L) were present as additives. Single metal deposition was used to determine the partial current densities from a similar electrolyte and was compared to the alloy partial current densities. The complexing agent, tartrate, and the additives were necessary to produce smooth deposits in all elemental and alloy depositions.

All studies were carried out on a rotating disk electrode (RDE) at 1000 rpm. The potential was measured and corrected for ohmic drop with impedance spectroscopy. The composition of the deposits was analyzed with a Kevex Omicron XRF. Twenty points were taken along the disk diameter for each sample and the geometric average was reported. A reproducibility analysis suggested that the deviation of composition is less than $\pm 3\%$. 
A square-wave pulse scheme was used in galvanostatic pulse plating, between a high and zero current. The period of the zero current was fixed at 5 seconds, and the high current pulse varied.

4.4 Results and Discussion

4.4.1 Steady State Results

Before the electrochemical investigation of the system was carried out, the effect of current distribution on the RDE was experimentally examined. Figure 4-1 shows the distribution of the contents of Co and Ni along the disk diameter for an alloy deposited at –70.7 mA/cm² and 1000 rpm. Three replicates were fabricated, and for each 20 points were analyzed. Edge effects were obviously observed, but it is restricted in a region of about 1/10 of the diameter. The composition is confirmed to be highly uniform for most of the electrode area. At the edge, the content of Co drops and Ni increases.

Figure 4-1: Contents of (a) Co and (b) Ni in three duplicates of alloy deposited at 1000 rpm and –70.7 mA/cm² along the disk diameter due to the effect of current distribution.
Steady state experiments were carried out to characterize the electrolyte system (See Chapter II). The interaction effect of each metal ion deposition rate due to the presence of other metals was simulated by the model at 1000 rpm and compared to experimental data. The partial current densities of the four metal elements, deposited from a single solution and from the alloy system, are presented in Figure 4-2.

As shown in Figure 4-2, the deposition rates of Ni, Co and Cu in the kinetic regime were inhibited in the alloy solution compared to their single metal rates, similar to the data at 2000 rpm presented in Chapter II. In contrast, the deposition rate of Fe is larger when it is deposited as an alloy than its elemental deposition, also observed in Figure 2-10. The Cu deposition was not expected to alter the iron-group metal deposition rates, but its rate is affected by the presence of the latter. An explanation for the change in Cu current density is that there is less free surface area due to the adsorption of predominately Fe intermediates, which is also consistent with an apparent inhibition of the Ni and Co rates. However the limiting current densities of these
species, which depend on their concentrations in the electrolyte and the electrode rotation rate, were unchanged.

Figure 4-2: Experimental partial current densities of (a) Ni, (b) Co, (c) Fe and (d) Cu, for alloy deposition (+) and for their own elemental depositions (■), in comparison with the simulation results (alloy: - - -; elemental: ——), at 1000 rpm.
Simulated partial current densities are also presented in Figures 4-2, and match the experimental results well. The diffusion coefficients used in the model simulation are listed in Table 4-1. Diffusivities of metal ions and the proton were determined by matching the
experimental limiting current densities. These values differ from literature ones\cite{39} due to the presence of the complex agent in the solution. For oxygen and hydroxyl anion, literature values were assumed.\cite{39} Since the oxygen concentration is sensitive to N\textsubscript{2} sparge and exposure to air, (see Chapter II) the concentration of oxygen was determined from its limiting current density, and a constant of 0.15 mM was found.

**Table 4-1.** Diffusion coefficients of species at room temperature (ion species can be complexed with additives).

<table>
<thead>
<tr>
<th>Species</th>
<th>$D$ ($cm^2/s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe\textsuperscript{++}</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Co\textsuperscript{++}</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Ni\textsuperscript{++}</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>Cu\textsuperscript{++}</td>
<td>$3 \times 10^{-6}$</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>$2.42 \times 10^{-5}$</td>
</tr>
<tr>
<td>H\textsuperscript{+}</td>
<td>$6.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>OH\textsuperscript{-}</td>
<td>$5.273 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

In the range of cathodic deposition at steady state, anodic reactions are neglected in the simulation. Kinetic constants used for reduction of metals are listed in Table 4-2. Table 4-3 shows the constants for side reactions. The side reaction rate differs considerably in different solutions, which was simulated by changing the kinetic parameters for proton and water reduction. This is consistent with the catalytic variability between different metal surfaces.\cite{40}

The side reaction in the alloy system is presented in Figure 4-3. It is composed of three parts. The first plateau between -0.25 to -0.6 V is the reduction of oxygen, which was verified by changing the amount of N\textsubscript{2} sparged into the solution (see Figure 2-8). Proton reduction governs the second part, which reaches its limiting current density at around -0.9 V. The last part is the reduction and dissociation of water, which becomes dominant after about -1.1 V.
Figure 4-3: Experimental (■) and simulated (—) side reaction current density in the FeCoNiCu alloy system at 1000 rpm.

Table 4-2. Kinetic constants of metal reduction reactions, with unit of k: *, cm/sec; **, cm$^{4}$/mol·sec; ***, mol/(sec·cm$^{2}$); and unit of b: 1/V.

<table>
<thead>
<tr>
<th>Reaction k</th>
<th>$k^0$</th>
<th>b$_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{++}$ + e$^-$ → Fe$_{ads}^+$</td>
<td>2.5 × 10^{-11}</td>
<td>*</td>
</tr>
<tr>
<td>Fe$_{ads}^+$ + e$^-$ → Fe</td>
<td>8.0 × 10^{-17}</td>
<td>***</td>
</tr>
<tr>
<td>Co$^{++}$ + e$^-$ → Co$_{ads}^+$</td>
<td>3.0 × 10^{-12}</td>
<td>*</td>
</tr>
<tr>
<td>Co$_{ads}^+$ + e$^-$ → Co</td>
<td>5.0 × 10^{-11}</td>
<td>***</td>
</tr>
<tr>
<td>Ni$^{++}$ + e$^-$ → Ni$_{ads}^+$</td>
<td>4.0 × 10^{-10}</td>
<td>*</td>
</tr>
<tr>
<td>Ni$_{ads}^+$ + e$^-$ → Ni</td>
<td>1.5 × 10^{-14}</td>
<td>***</td>
</tr>
<tr>
<td>Cu$^{++}$ + 2e$^-$ → Cu</td>
<td>1.0 × 10^{-8}</td>
<td>*</td>
</tr>
<tr>
<td>Fe$^{++}$ + Co$^{++}$ + e$^-$ → FeCo$_{ads}^{+++}$</td>
<td>1.0 × 10^{-15}</td>
<td>**</td>
</tr>
<tr>
<td>FeCo$<em>{ads}^{+++}$ + e$^-$ → Fe + Co$</em>{ads}^{++}$</td>
<td>3.0 × 10^{-10}</td>
<td>***</td>
</tr>
<tr>
<td>Fe$^{++}$ + Ni$^{++}$ + e$^-$ → FeNi$_{ads}^{+++}$</td>
<td>1.4 × 10^{-5}</td>
<td>**</td>
</tr>
<tr>
<td>FeNi$<em>{ads}^{+++}$ + e$^-$ → Fe + Ni$</em>{ads}^{++}$</td>
<td>6.4 × 10^{-16}</td>
<td>***</td>
</tr>
<tr>
<td>Co$^{++}$ + Ni$^{++}$ + e$^-$ → CoNi$_{ads}^{+++}$</td>
<td>4.0 × 10^{-7}</td>
<td>**</td>
</tr>
<tr>
<td>CoNi$<em>{ads}^{+++}$ + e$^-$ → Co + Ni$</em>{ads}^{++}$</td>
<td>3.4 × 10^{-16}</td>
<td>***</td>
</tr>
</tbody>
</table>
Table 4-3. Kinetic constants of side reactions, with unit of k: *, cm/sec; **, mol/(sec·cm²); ***, mol/(sec·cm²) · (cm³/mol)⁵, and unit of b: 1/V.

<table>
<thead>
<tr>
<th>Reaction k system</th>
<th>system</th>
<th>$k_0^i$</th>
<th>b&lt;sub&gt;k&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$</td>
<td>**</td>
<td>1.0 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
<td>54.49</td>
</tr>
<tr>
<td>$H^+ + e^- \rightarrow H_{ads}$</td>
<td>Fe</td>
<td>2.0 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>7.78</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>5.0 × 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>7.78</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>2.0 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>7.78</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>2.0 × 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>7.78</td>
</tr>
<tr>
<td></td>
<td>Alloy</td>
<td>1.5 × 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>13.62</td>
</tr>
<tr>
<td>$H_{ads} + H_{ads} \rightarrow H_2$</td>
<td>Fe</td>
<td>2.0 × 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>1.0 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>6.0 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>2.0 × 10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Alloy</td>
<td>5.0 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>0</td>
</tr>
<tr>
<td>$H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^-$</td>
<td>Fe</td>
<td>4.0 × 10&lt;sup&gt;-13&lt;/sup&gt;</td>
<td>9.73</td>
</tr>
<tr>
<td></td>
<td>Co</td>
<td>1.3 × 10&lt;sup&gt;-12&lt;/sup&gt;</td>
<td>9.73</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>2.0 × 10&lt;sup&gt;-13&lt;/sup&gt;</td>
<td>9.73</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>2.0 × 10&lt;sup&gt;-15&lt;/sup&gt;</td>
<td>9.73</td>
</tr>
<tr>
<td></td>
<td>Alloy</td>
<td>4.5 × 10&lt;sup&gt;-11&lt;/sup&gt;</td>
<td>9.73</td>
</tr>
</tbody>
</table>

Figure 4-4 shows the simulated and experimental current efficiencies in the alloy system. The efficiency is very low at less negative potentials because of the reduction of oxygen, and it increases as the reduction of Cu becomes gradually significant. After Cu reduction becomes mass transport controlled, proton reduction takes place, and the efficiency drops again. Once the hydrogen partial current density approaches its limiting value, the efficiency increases as the iron-group metal reduction rates increase with potential. However, at very high overpotentials, the reduction of water dominates and the efficiency again becomes very low.
Figure 4-4: Simulated results (---) of the steady state current efficiency for the alloy system compared with experimental data (■).

Figure 4-5 shows the results of the deposit composition from the steady state simulation, which agrees with experiments well as a consequence of the partial current density fit. As expected, at low current density pure copper is deposited, and at high current the deposit becomes a Co-rich alloy. A maximum of Fe content is predicted, similar to other experimental studies,[42] a characteristic of anomalous codeposition. The decrease in the Fe content is accompanied by an increase in Ni content, with the Co concentration staying relatively constant. At potentials more negative than –0.4 V, the copper deposition is at its limiting current and the partial current density is a constant. As the overpotential becomes higher, the deposition rate of the iron group metals increases, and the Cu content decreases.

Simulation was also performed for steady state plating processes in solutions with different concentrations. Figure 4-6 shows simulations of the deposit composition versus the applied current density as the concentrations of the metal ions change. The decrease of Fe concentration in the solution increases the content of the other three metals in the deposit, but not
Figure 4-5: Simulated result (Fe: --; Co: ••••; Ni —; Cu - - -) and experimental data (Fe: ○; Co: ■; Ni: ●; Cu: +) of steady state deposit composition for alloy system.

significantly (Figure 4-6(a)). The maximum of Fe content in the deposit decreases with the Fe concentration in the solution, indicating the lower inhibition effect of Ni and Co by Fe.

The increase of the Co and Cu concentration in the solution increases the content of the corresponding metal in the deposit, and decreases the other three (Figure 4-6 (b) and (d)). The same trend was observed Ni. A higher Ni concentration increases the Ni content in the deposit. It also increases the Co content significantly (Figure 4-6(c)). This is believed to be due to the enhancement effect of the Ni$^{2+}$ on the Co plating, as observed in binary and ternary systems.$^{[22,38]}$

As more Ni$^{2+}$ is present in the solution, the catalytic step for Co plating, as sketched in Equations 4-10 to 4-13, contributes more, and thus increases the Co plating rate.

A maximum was observed for Co content as the Ni concentration increases to as high as five times the original concentration. The mechanism is the same as the Fe content maximum. In the kinetic controlled potential region, the deposition of Fe or Co is preferred rather than Ni due to the preferably adsorbed Fe or Co intermediate species. When the potential is high enough, the
plating rate of Fe or Co becomes mass transport controlled, and the intermediates are depleted. The Ni plating then increases, and the content of Ni increases, resulting in a decreasing of Fe or Co. However, in the original solution, the Co maximum was not observed, because the Ni concentration was not high enough to achieve the high Ni plating rate in the range of current densities studied.

**Figure 4-6**: Simulated deposit composition, (—) Fe, (···) Co, (- - -) Ni, and (— —) Cu, at different current densities for original solution and solutions with various concentrations of (a) Fe; (b) Co; (c) Ni; and (d) Cu.
4.4.2 Non-steady State Results

The kinetic constants from the steady state simulation for the alloy system were used in the simulation for the non-steady state deposition at a constant current of -35.4 mA/cm², which is the condition that yielded multilayers with GMR properties in Chapter III and a previous publication. A series of pulses, between –35.4 mA/cm² and zero current, was also performed. The off-time was fixed at 5 seconds, and by varying the on-time, the resulting composition...
measurements can be used to mimic the composition profile of nano-layers during non-steady state deposition.

Figure 4-7 shows the simulation results of the relaxation of the electrolyte concentration profiles during the zero current pulse for \( \text{Cu}^{2+} \) and \( \text{H}^+ \) in alloy solution. The diffusion coefficients in Table 4-1 were used in the simulation, and the initial concentration profiles were obtained from a simulation of a steady state alloy deposition at high current pulse, \(-34.5 \text{ mA/cm}^2\). For all the species, including the species not shown, within a relaxation time of 1 second, the concentration at the electrode surface has been restored to 99% of the bulk concentration. Therefore, the off-time period, 5 seconds, was long enough for the electrolyte concentration profiles developed during the high current pulse to relax and the bulk concentration to be restored everywhere in solution.

![Figure 4-7](image-url)

**Figure 4-7**: Simulated result of the relaxation of the (a) \( \text{Cu}^{2+} \) and (b) \( \text{H}^+ \) concentration profile in the solution during a zero current pulse.
The simulation results presented in Figures 4-8 to 4-10 report the composition at different pulsing on-times. The x-axis is represented as thickness, which is the effective thickness of a single on-pulse, taking the current efficiency into account. Thus, the choice of x-axis also renders it useful to simulate the change of the composition through an interfacial region of a compositional multilayer.

Figure 4-8(a) shows the experimental results and the model prediction of the alloy composition for pulse plated alloys. The model assumed no corrosion or displacement reactions in this simulation. Due to the non-steady characteristics of pulse plating, the copper content decreases as its concentration at the electrode surface depletes. Therefore, as the deposition time increases the content of iron-group metals increases until the steady state values are achieved. Experimental data suggested that the deposition region reaches steady state after about 1 second,
equivalent to a layer thickness of about 3 nm. However, the model underpredicts the end of the transient region of concentration without displacement reactions. The simulated composition approaches its steady state value after about 0.23 second, equivalent to 0.5 nm in thickness. Furthermore, the predicted steady state content is systematically larger for cobalt and lower for copper.

The observed discrepancy between the simulation and experimental data suggests that anodic reactions are nontrivial in the off-time for a pulse scheme. There are two possible displacement mechanisms with copper reduction that were assumed to occur when the current is zero, i.e., oxidation of adsorbed intermediates of iron group metals and ii. solid cobalt metal displacement, according to Equations 4-29 to 4-32.

\[
\begin{align*}
\text{Co}^{+} & \text{ads} + \text{Co}^{+} \text{ads} + \text{Cu}^{+} \rightarrow \text{Co}^{++} + \text{Co}^{++} + \text{Cu} & \text{Eq. 4-29} \\
\text{CoNi}^{++} \text{ads} + \text{CoNi}^{++} \text{ads} + \text{Cu}^{+} & \rightarrow 2 \text{Co}^{++} + 2 \text{Ni}^{++} + \text{Cu} & \text{Eq. 4-30} \\
\text{FeNi}^{+++} \text{ads} + \text{FeNi}^{+++} \text{ads} + \text{Cu}^{+} & \rightarrow 2 \text{Fe}^{++} + 2 \text{Ni}^{++} + \text{Cu} & \text{Eq. 4-31} \\
\text{Co} + \text{Cu}^{++} & \rightarrow \text{Co}^{++} + \text{Cu} & \text{Eq. 4-32}
\end{align*}
\]

The quantity of adsorbed species are determined at the last time step during the high current pulse and converted into the equivalent amount of copper metal during the off-time. It was assumed that the off-time is sufficient for complete displacement at one monolayer.

Figure 4-8(b) shows the simulated composition profile with displacement included, compared with experimental data. The simulation matches the data better than Figure 4-8(a),
which doesn’t include displacement. Comparison of the simulation in Figures 4-8 (a) and (b) shows a large difference in the region within 3 nm.

Figure 4-8: Simulated composition gradient of the pulsed plated alloys, (a) without and (b) with displacement (Fe: ---; Co: · · ·; Ni ---; Cu - - -) in comparison with experimental data (Fe: ○; Co: ■; Ni: ●; Cu: +. The pulse current is between –35.4 mA/cm² and zero current.
Figures 4-9 (a) and (b) show another pair of simulated and experimental results for a galvanostatic pulse between -70.7 mA/cm$^2$ and zero current, without and with displacement included. The experimental results confirm the model prediction similar to the case when the pulse current was -35.4 mA/cm$^2$.

**Figure 4-9:** Simulated composition gradient of the pulsed plated alloys, (a) without and (b) with displacement (Fe: -·-·-; Co: · · · ·; Ni —; Cu - - -) in comparison with experimental data (Fe: ○; Co: ■; Ni: ●; Cu: +). The pulse current is between −70.7 mA/cm$^2$ and zero current.
Since the bulk alloys were fabricated by stacking nanometer thick deposits, they can also be used as a guideline to estimate the concentration transients within a nanometric alloy layer in compositionally modulated films, without the extensive vacuum analytical techniques (i.e. TEM, AES with depth profiling) and without the cost to do such an analysis in highly localized regions. Inclusion of the corrosion reactions in the model represent an upper limit in the transient interfacial region, while the elimination of them sets the lower bound.

In fabrication of FeCoNiCu/Cu multilayers,[13] the current was pulsed between –35.4 mA/cm\(^2\) and –0.354 mA/cm\(^2\). The partial current densities in Figure 4-2 show that, during the lower current pulse, the deposition of the copper layer was under a mixed kinetic-diffusion control. Since the time for the lower current was on the order of 100 seconds, the electrolyte concentration at the electrode surface is believed to be nearly restored to the bulk concentration at the end of off-time, or the start of next high pulse.

Deposition of layers through a displacement mechanism at zero current is expected to yield a monolayer of Cu of 0.23 nm at 1000 rpm on the RDE from the electrolyte presented here. Multilayers produced in this manner have also been shown to exhibit a change of resistance in a magnetic field.[43] However, the layer thickness of Cu that is obtained in this study via displacement is far from the values that optimize the GMR property.[44]

The results of a series of pulsed simulations at a current density of -35.4 mA/cm\(^2\) at different rotation rates are presented in Figure 4-10. The depicted copper concentration decreases as a function of the pulse length. In a compositionally multilayered alloy, the x-axis can be treated as the distance from the interfacial region between the more noble and less noble layers. Thus, at 1000 rpm, a compositional gradient region occurs within 2 nm of the more noble layer thickness in a multilayered alloy, while the transient spans a thickness larger than 5 nm at 8000
rpm. To summarize the results, the thickness of the transient region, $d_{\text{grad}}$, in nm units, was fit to a power relation of the Levich boundary layer thickness [34] for copper, $\delta_{\text{Cu}}$, in μm units:

$$d_{\text{grad}} = 466.8 \cdot \delta_{\text{Cu}}^{-1.8} \quad (\text{with } R^2 = 0.944)$$

Eq. 4-33

The end of the transient region was determined at a thickness where 95% of the steady state value was achieved. The coefficients in Equation 4-33 were determined from the slope and intercept of a linear least squares fit of the natural log of $d_{\text{grad}}$ (generated by the model) versus the natural log of $\delta_{\text{Cu}}$.

![Figure 4-10: Simulated copper deposit concentration gradient, at different rotation rates, of the pulsed plated alloys (----) without and (—) with displacement at –35.4 mA/cm$^2$.](image)

4.5 Summary

Electrodeposition of the FeCoNiCu system was studied and a model was developed to tailor the composition gradient under a nonsteady state deposition with a high current pulse.
Anomalous codeposition was simulated well for steady state plating, and the deposition of copper was also affected by the presence of adsorbed iron group intermediates. A displacement mechanism was needed to account for the iron group corrosion during the off pulse time determined by comparing model predictions with the experimental analysis. The simulation suggested that the compositional gradient within the alloy layer does not exceed a thickness of 3 nm at 1000 rpm. An empirical correlation relating the transient region as a function of the boundary layer thickness to the $-1.8$ power was determined from the simulation results.

4.7 References


5.1 Introduction

A nanowire, which refers to a wire structure having a diameter on the nanometer scale, has recently attracted much research attention. Arrays of nanowires have potential applications in perpendicular ultra-high density data storage\cite{1} and biosensors\cite{2}. In addition, they also provide good candidates for studies on magnetic shape anisotropy, and magnetic coupling\cite{3,4}. Furthermore, when the nanowire is composed of multilayer structures of ferromagnetic and nonmagnetic layers, it allows the study of perpendicular magneto-transport phenomena, such as magneto-electric resistance (MR) and magneto-thermal conductance\cite{5,6}.

Compared with the so called giant magnetoresistance (GMR) in multilayer thin films, where the electric current is in the layer plane (CIP), the MR of nanowire with current perpendicular to the plane (CPP-GMR) is expected to be much larger\cite{5,6}. In CIP-MR, the characteristic scaling length is the electron mean-free path, which is a few nanometers. In contrast, in CPP configuration, the critical length scale is the spin diffusion length, which is dependent on temperature and is generally larger than 10 nm\cite{7,8}. GMR has been observed in multilayer nanowires having a layer size of 12 nm NiFe / 4 nm Cu\cite{9} and 5 nm Co / 8 nm Cu\cite{10}, larger than typical thin film multilayers. Even a small MR effect was still observed in multilayer nanowires with a magnetic layer thickness of about 1 \(\mu\)m,\cite{5,6} while the GMR of multilayer thin films vanishes when the layer thickness exceeds a few nanometers.

In addition to the advantages of high deposition rate, and low capital cost in investment and operation, electrodeposition is a superior method for deposition into curved and recessed
areas, of which nanowire fabrication is a perfect application. The electrodeposition of nanowires involves a nonconductive template with nanometric holes. After the deposit fills up the holes, the nanowires are released from the template by dissolving it in an appropriate solution. Two types of templates have been used most widely, anodic aluminum oxide (AAO) and polycarbonate membranes. The AAO membrane can be prepared with an application of anodic current or potential on aluminum foil in sulfuric acid solutions. The pore size can be well-controlled by the current or potential applied, and the pores can be well-ordered in a hexagonal configuration.[11,12] In contrast, the polycarbonate membranes are usually prepared with a nuclear track etch process,[13] and the pore size can be much smaller than the AAO. However, some misalignment by up to 30° was observed and was believed to affect the magnetic coercivity of the nanowires array.[14,15] Another method for template preparation is by using the self-assembly of diblock copolymers. Tuominen’s group[16,17] selectively removed one part of the self-assembled polystyrene-methyl methacrylate copolymers, and a hexagonally packed porous template were fabricated.

Nanowires of different pure metals and alloys have been electrodeposited and studied.[3,4,18-26] Garcia et al.[4] studied the magnetic behavior of an array of Co nanowires plated in AAO membrane. They found that the axis of the wire is the easy axis of magnetization, and a maximum of the coercivity was found perpendicular to the easy axis. These features are explained by the magnetic coupling among the nanowires. They simplified the nanowire interactions, and simulated the coercivity minimum along the wire direction. This easy axis direction was also observed in Fe[19], CoNi[22] and CoFe[23,25] nanowires, however with an enhanced coercivity. Rivas et al.[3] studied the Co nanowires plated in polycarbonate membranes, and found a magnetization reversal that depends on the wire length. The easy axis is along the wire with a short wire length, and when the length becomes longer, a crossover of magnetization
was observed. The results were successfully explained with the inclusion of a demagnetization field, shape anisotropy, and the dipolar coupling among nanowires.

Since electrodeposition was adopted in fabrication of GMR multilayer thin films, nanowires of multilayers have also been studied for a few systems, but with limited effort, thus far, and larger GMR effects were observed at room temperature compared to the thin film case. Piraux et al.\textsuperscript{[27]} studied the CPP-GMR of Co/Cu multilayer nanowires with a MR value about 15 \% found at room temperature. The MR at 4 K was found to be almost the same as its room temperature value, which is also observed in this system by other authors.\textsuperscript{[7,9,28]} Blondel et al.\textsuperscript{[29]} and Schwarzacher et al.\textsuperscript{[30]} studied CoNi/Cu nanowires, and one of the highest electrodeposited GMR at room temperature was observed for this system, as 55\%.\textsuperscript{[30]} NiFe/Cu multilayer nanowires were fabricated by Dubois et al.,\textsuperscript{[8]} and were found to exhibit 20 \% GMR at ambient temperature and about 80 \% at 4 K. This system was also studied by Blondel et al. with a however lower GMR observed.\textsuperscript{[28]}

Despite the numerous research efforts on nanowire deposition for different systems, few studies have been carried out on alloys and multilayers for alloy systems containing more than two elements. To our knowledge, no study has been performed in the FeCoNiCu system. In this chapter, electrodeposition conditions for nanowires are explored for the fabrication of FeCoNiCu alloy nanowires and FeCoNiCu/Cu multilayer nanowires.

Different from the thin film plating on RDE, the plating in deep recessed templates is controlled by mass transport in most cases due to the large diffusion distance. Therefore, during pulse deposition, the control of the deposit composition needs to take into consideration the transient processes. In addition, the nanometric size of the recess structure exaggerates the problem caused by side reactions. Small hydrogen bubbles generated from proton reduction will
easily block the recess hole. In addition, a pH increase is expected in the recess holes due to hydrogen evolution, which might cause the precipitation of metal hydroxide and cease the wire growth.

5.2 Experimental

Three alloy baths with different cupric ion concentrations, as listed in Table 5-1, were explored for nanowire deposition. The electrolytes are more concentrated than the multilayer thin film plating electrolytes (see Chapter III) to improve current efficiency. The concentration of iron-group metals is always much higher than Cu, in order to plate the magnetic layer containing a minimum of Cu. Nickel sulfamate is used instead of sulfate, considering the well-known success of sulfamate bath in deep recess plating and producing low-stress deposit.\(^{[31]}\)

Table 5-1. Composition of different solutions for nanowire plating.

<table>
<thead>
<tr>
<th></th>
<th>Bath 1</th>
<th>Bath 2</th>
<th>Bath 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO(_4) 7H(_2)O (mol/L)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>CoSO(_4) 6H(_2)O (mol/L)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Ni(SO(_3)NH(_2))(_2) 6H(_2)O (mol/L)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>CuSO(_4) 5H(_2)O (mol/L)</td>
<td>0.01</td>
<td>0.03</td>
<td>0.003</td>
</tr>
<tr>
<td>NaKC(_4)H(_4)O(_6) 4H(_2)O (mol/L)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Triton X-100 (g/L)</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>pH</td>
<td>Natural pH = 3.3</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

AAO (Whatman®) membrane was used as the template for nanowire plating. The pore size varied, from about 100 nm to 200 nm, and was determined from scanning electron microscope (SEM) examination of the nanowires after plating. A schematic of the process is shown in Figure 5-1. Figures 5-1 (a) and (b) illustrate an AAO template before and after a layer of Au is sputtered on one side as conductive substrate. As the plating proceeds, the wires grow in
the pores and fill the pores at the end of plating, as shown in Figure 5-1 (c). Figure 5-1 (d) shows
the nanowire released from the template after the AAO is dissolved in a 1 M NaOH solution.

![Figure 5-1](image)

**Figure 5-1.** Steps for template plating of nanowires: (a) template, (b) Au sputtering, (c) plating,
and (d) dissolution of template to release nanowires.

As illustrated in Figure 5-2, the holder for the plating is composed of two pieces. The
upper piece has a 10-mm-deep opening with the template placed underneath. The sputtered Au
layer on the backside of the template contacts a Cu plated that is connected to a wire through the
back. Two O-rings were used to seal and clamp the top of the membrane, preventing electrolyte
leakage and undesired plating.

![Figure 5-2](image)

**Figure 5-2.** Holder for nanowire plating, with opening size of 1.5 cm × 1.5 cm.
The plating was carried out without agitation. A platinum mesh was used as anode, and a saturated calomel electrode (SCE) was used as potential reference. A PINE bipotentiostat controlled by computer, with an Amel 5683 function generator, was used to provide the pulse schemes.

A JEOL JSM-840A SEM, operated at 20 kV, was used to inspect the nanowire. Qualitative composition analysis was obtained with an energy dispersive X-ray (EDX) detector option on the SEM. Wavelength dispersive X-ray spectroscopy (WDS) was used for quantitative analysis. Detailed structure of the wire was examined with a JEOL JEM-2010 transmitted electron microscope (TEM) operated at 200 keV with a point-to-point resolution of 2.3 Å.

5.3 Results and Discussion

An AAO membrane cross sectional structure was pre-checked using SEM with 20 nm Au sputtered as a conductive layer. As shown in Figure 5-3, the membrane thickness was 60 µm, and the pore diameter was about 100 nm with pore-to-pore separation of about 350 nm. The pore size was found much larger than the specification, 20 nm, probably because the quoted value came from the effective size for filtration, or the minimum size along the pore.

5.3.1 Cu Nanowire

Baths 1 and 2 were investigated for alloy nanowire plating in AAO membranes with a DC potentiostatic method. Figure 5-4 presents the SEM micrograph and EDX spectrum of nanowires plated in Bath 1 at a constant potential of –0.5 V versus SCE. Estimated from the SEM micrograph in Figure 5-4, the diameter of the nanowires is about 100 nm, consistent with the AAO membrane examination. The length is about 15 µm, much shorter than the thickness of AAO membrane. EDX spectrum, in Figure 5-4 (c) shows that the nanowire plated at this
potential is a Cu-rich alloy with a trace of Co. Therefore, the potential was a little too negative to yield a pure Cu deposit.

Figure 5-3. SEM micrograph of the cross section structure of an AAO membrane.

Figure 5-4. Nanowires plated with AAO in Bath 1 at –0.5 V versus SCE, (a) SEM side view image; (b) top view image; and (c) EDX spectrum.
Figure 5-5 shows the current responses during the plating of the nanowires shown in Figure 5-4. An increase in current was observed after 20000 seconds, or about 6 hours, until a steady large value was reached. This is a characteristic profile when the pores are filled. As more and more pores are filled completely, the current increases gradually until all pores are filled and reduction occurs on top of the AAO template. At this point, the total area increases and thus the current goes up. However, the length of the nanowires observed here in Figure 5-4 (a) is much less than the thickness of the template (see Figure 5-3). A red porous deposit was found on top of
the template after the plating was stopped. Therefore, the plating did fill the pores, although the latter part of the wire had such a poor structure that it fell apart when the membrane was removed. The porous deposit is believed to be due to the side reactions occurring in the metal deposition. Firstly, hydrogen from the side reactions may be included in the deposit. Secondly, metal hydroxide can precipitate at a high pH resulting from the side reactions. This ‘crispy’ part of the deposit is weak and cannot be sustained once the template is dissolved, resulting in the much shorter length of Cu nanowires than the thickness of AAO membrane.

Figure 5-5. Current response of nanowire plating with AAO in Bath 1 at potential –0.5 V versus SCE.

In order to avoid the severe side reaction effect in Cu plating, a higher Cu concentration bath was used, Bath 2. Potentiostatic DC plating at –0.5 V versus SCE failed in producing fully-grown Cu nanowire again. A lower potential of –0.3 V was used to suppress the proton reduction, and the iron-group deposition. The current response was recorded in Figure 5-6. The lowest current, -0.6 mA, is believed to be the limiting current when the pore is empty. After the
beginning period, as the concentration gradient along the pores is established, the current increases gradually in the whole plating period, as sketched in the figure. A steady state value of high current was reached after 60000 seconds, which corresponds to the filling of the pores. The deposit has a solid Cu layer on top of the template after plating, unlike the porous deposit obtained when the Cu plating potential was too high at –0.5 V.

**Figure 5-6.** Current response of nanowire plating with AAO in Bath 2 at potential –0.3 V versus SCE.

Figure 5-7 is the SEM micrograph and EDX spectrum of the nanowire plated from Bath 2 at –0.3 V versus SCE. The wires are grown fully, with a length of about 35 µm and a mushroom-like overcover, shown in Figure 5-7 (a). The length is different from the AAO membrane shown in Figure 5-3, 60 µm, which suggests a variation in template thickness. EDX spectrum, Figure 5-7 (b), shows a higher purity of Cu compared to the previous case shown in Figure 5-4 (c), due to a lower potential applied.
Figure 5-7. (a) SEM micrograph and (b) EDX spectrum of nanowire plated with AAO in Bath 2 at potential –0.3 V versus SCE.

5.3.2 FeCoNiCu Magnetic Alloy Nanowire

A higher potential was used to deposit alloy nanowires rich in iron-group elements from the quaternary system. Figure 5-8 presents the SEM micrographs with EDX spectrum of nanowires plated at a constant potential of –1.0 V versus SCE, from Bath 1. The plating time was 2.5 hours, and the nanowires were found to grow fully within the template, producing a mushroom-like cap on top. The length of wire was about 60 µm and the diameter, determined
from the enlarged micrograph in Figure 5-8 (b), is around 200 nm. The difference in the diameter from the Cu nanowire in Figure 5-4 suggests a variation in the pore size of AAO.

The EDX shows that the nanowire is a Co-rich alloy. WDS analysis of a duplicate gives a composition as Fe\(_{20.5}\)Co\(_{66.1}\)Ni\(_{8.9}\)Cu\(_{4.5}\). The magnetic hysteresis was checked at the directions parallel and perpendicular to the wires. Figure 5-9 shows the magnetization hysteresis loop. An easy axis was found parallel to the nanowires, with a saturation field about 5000 Oe, consistent with studies on other magnetic nanowires.\(^{[3,4,19-25]}\)

**Figure 5-8.** Nanowires plated with AAO template in Bath 1 at –1.0 V versus SCE for 2.5 hours: (a) SEM overview image; (b) enlarged micrograph; and (c) EDX spectrum.
Plating was also carried out in Bath 2 at a constant potential of \(-1.0\) V versus SCE. The micrograph and EDX spectrum of the nanowires are shown in Figure 5-10. A higher content of Cu was found than the one previously plated in Bath 1 (see Figure 5-8) as expected from higher Cu\(^{2+}\) concentration in the electrolyte. The nanowire was not fully grown, about 25 \(\mu\)m, while the current reached a high steady state value after about 1.5 hours, indicative of a significant side reaction. This inconsistence in the full growth of wire with the one shown in Figure 5-8, is presumably due to the variation of the AAO membranes.

**Figure 5-9.** Hysteresis loop of nanowire DC plated in Bath 1 at \(-1.0\) V versus SCE, examined at direction of (·····) parallel and (——) perpendicular to the nanowires.
Based on the above DC potential plating investigations, double potentiostatic pulse schemes were explored for making multilayer nanowires of FeCoNiCu/Cu, as shown in the sketch, Figure 5-11. In potential pulses, at the beginning of the low potential pulse, the initial current jumps to an anodic value due to the low surface concentration of the metal ions resulting from the prior high potential pulse. In some extreme cases, the anodic current is so high that it dissolves the deposit plated in the prior step completely. In order to get around this problem,
different low potential pulses were investigated. The charge in the anodic current has to be less compared with the charge in the high potential pulse.

![Figure 5-11. Sketch of a double potential pulse scheme for multilayer plating.](image)

Pulse plating was performed in Bath 1, with $-1.0 \text{ V}$ for 30 seconds and $-0.55 \text{ V}$ for 500 seconds. Although the Cu plating in Bath 1 at $-0.5 \text{ V}$ turned out to be not as good as $-0.3 \text{ V}$, this higher potential value helped to prevent the current from being completely anodic during the transient region of the pulse, which is not evident with steady state, DC plating. In addition, the pulse sample was plated before the results of the pure Cu layer were obtained. Therefore, in hindsight these pulse parameters are not the most desirable. Nevertheless, the data is shown here to establish a base case. Figure 5-12 presents the current response and integrated charge, where the response is steady. The anodic current was observed, and the dissolution charge from the anodic current is small compared with the deposition charge in the high potential pulses.

Figures 5-13 shows the SEM image of the nanowires. The nanowires were about 15 $\mu$m long, with diameter of 180 nm. Selective etching was performed with $\text{HNO}_3/\text{C}_2\text{H}_5\text{OH}$ (volumetric ratio 1:20) solution for 3 minutes to increase the image contrast. As studied in chapter VI, Co-rich alloy is etched favorably. The layer structure was observed after etching, but the layer thickness was significantly smaller than the calculation.
Figure 5-12. (a) Current response and (b) total charge of nanowire plating with AAO in Bath 1 at potential –1.0 V, –0.55 V versus SCE for 30 and 500 seconds, respectively.

EDX spectrum, as in Figure 5-14, shows a considerably higher Cu content than Co-rich alloy nanowire shown in Figure 5-8, as expected, due to the layering. An average atomic composition of 15.7 % Fe, 47.0 % Co, 7.3 % Ni, and 30.0 % Cu was obtained with WDS analysis. The Co-rich alloy is estimated to be about 2.7 times thicker than Cu layer from the average composition. Since a thickness of about 170 nm was determined from Figure 5-13 (b)
for a bilayer (one Cu layer and one Co-rich alloy layer), the actual multilayer fabricated was Cu\text{46} nm / FeCoNiCu\text{124} nm.

![Figure 5-13](image)

**Figure 5-13.** SEM micrographs of nanowires plated with AAO template in Bath 1 with potential −1.0 V, −0.55 V versus SCE for 30 and 500 seconds, (a) as deposit, (b) after selective etching in HNO₃/Ethanol for 3 minutes.

The deviation in Co-rich alloy layer thickness from the pre-calculation suggests that the effect of anodic current was still significant. Determined from Figure 5-12 (b), the charge in a single high current pulse is −0.52 A·s, and the charge in the following anodic current is 0.02 A·s. Assuming the plating during the high potential pulse is the same as the DC plating in Figures 5-4
Figure 5-14. EDX spectrum of nanowires plated with AAO template in Bath 1 at potential –1.0 V, –0.55 V versus SCE for 30 and 500 seconds.

and 5-8, the estimated layer thicknesses are 250 and 200 nm for Cu and Co-rich alloy layers, respectively. In comparison with the actual layer thicknesses, about 75 nm Co-rich alloy was dissolved resulting from the anodic current. Therefore, the efficiency in the high potential pulse plating can be approximated as about 10 %, indicative of a significant side reaction. An effective plating area of 0.1 cm$^2$, with an apparent area of 2.25 cm$^2$, can be obtained based on Faraday’s Law (Equation 5-1) with this efficiency. For a perfect hexagonal order of pores, the ratio of the pore-to-pore distance to the pore diameter is 4:1, consistent with the examination of the AAO membrane, shown in Figure 5-3.

$$\frac{-i \cdot t \cdot \varepsilon \cdot MW}{n \cdot F} = \rho \cdot d \cdot A$$

Eq.5-1

The actual Cu layer thickness is significantly smaller than the steady state calculation. The following reasons are believed to be responsible for this deviation. Firstly, the estimation of Cu layer thickness based on the nanowire in Figure 5-4 may not be accurate. Due to the low quality of the wire, the actual time for filling the holes is really unknown. An estimation based
on the Cu wire shown in Figure 5-7 gives a layer thickness of 97 nm in this plating scheme. Secondly, the actual plating time in the low potential pulse is less than the 500 seconds. Therefore, the apparent Cu deposition rate is considerably lower than in the DC plating case.

In order to get around the deviations from the anodic currents, galvanostatic pulses are used. In addition to the double galvanostatic pulse used in multilayer thin film deposition (see Chapter III), a relaxation period, or a zero current period, was added between the high current pulse for Co-rich alloy deposition and the following low current pulse for Cu layer deposition. A sketch is provided in Figure 5-15. The purpose of the relaxation pulse is to allow the hydrogen and hydroxide ions to diffuse out of the pores. Concurrently, the $\text{Cu}^{2+}$ ions are to diffuse into the pores as well. If the bulk concentration is restored throughout the pore at the end of relaxation period, each pulse is expected to be same as the first pulse.

![Figure 5-15](image)

**Figure 5-15.** Sketch of triple current pulse scheme, with a relaxation period, for multilayer nanowire deposition.

Whilst the galvanostatic method successfully avoids any anodic currents, it has its own inherent disadvantages. In a non-steady high current pulse, the partial current of the more noble metal, Cu, is higher than the steady state case due to the nonzero surface concentration before steady state is achieved. Concurrently, the partial current of the less noble iron-group metals is
lower from the restriction of the constant total current. Therefore, a deposit with much higher
content of Cu will be plated, as experimentally observed and predicted by the model for
multilayer thin films (see Chapter IV). In contrast, in a potentiostatic non-steady state region, the
iron-group metal partial currents will be increased, similar to Cu, thus still producing an alloy
that is less concentrated in Cu compared to the galvanostatic case.

In order to lower the Cu content in the Co-rich alloy layer, an electrolyte with lower Cu
concentration, Bath 3, was used. Figure 5-16 is the current response when a DC potential of –0.3
V versus SCE is applied. The current approached a steady value of –60 µA, 10 times lower than
the case in Figure 5-6, where a 10 times concentration of Cu\(^{2+}\) was present. This current is
believed to be the limiting current for Cu. The cupric ion was believed to be depleted at the
plating surface at this current, and the Cu\(^{2+}\) concentration gradient was established throughout
the pore length. With this limiting current applied in the low current pulse, no transient effect of
Cu is expected in the high current pulse when the wire is short, and the change in boundary layer
or the limiting current is negligible.

![Figure 5-16](image.png)

**Figure 5-16.** Current response of a DC potential of –0.3 V versus SCE with an AAO template in Bath 3.
Nanowires were plated with pulse conditions of –60 µA, -7.0 mA, and –2 µA for 30, 4 and 100 seconds, respectively. A tiny cathodic current was applied here in the relaxation period instead of zero, to avoid anodic dissolution from the current fluctuation due to the equipment limitation. A Cu layer thickness of 1.8 nm was estimated from the Cu nanowire shown in Figure 5-7. The Co layer thickness was estimated as 18 nm from the Co-rich alloy nanowire shown in Figure 5-10. The deposition lasted for 70 hours, or 1880 cycles. The estimated total length of the wire is 38 µm if the plating is the same as the DC cases and unchanged throughout the growth of nanowires.

An SEM micrograph and the EDX spectrum of the nanowires are shown in Figure 5-17. The length of the nanowires is about 22 µm, much less than the estimation, and the average thickness of one bilayer (one Cu layer and one Co-rich alloy layer) is calculated to be 12 nm. The composition was found to be different at the two ends of the nanowires from EDX spectrums. A higher Cu content was observed for the top end of the wires. This can be due to the reduced boundary layer thickness of the Cu.

A multilayer structure was observed from TEM analysis. Figure 5-18 presents a bright field image of the nanowires. As the micrograph of the multilayer thin film shows in Figure 3-6, the bright layer is Cu and the dark layer is Co-rich alloy. The layer thicknesses estimated from the micrograph in Figures 5-18 (a) are 2.5 nm for Cu and 8.0 nm for FeCoNiCu, resulting in a bilayer thickness of 11 nm, consistent with the estimation based on the total wire length. However, much thinner layer thicknesses, 1.8 nm Cu and 4.0 nm Co-rich alloy, were determined from the micrograph of another portion of the wires, shown in Figure 5-18 (b). The Cu layer thickness in this portion is consistent with the calculation from DC plating, indicating this part was plated at the bottom of the nanowires.
Figure 5-17. Nanowires plated with AAO template in Bath 3, at –60 µA, -7 mA, and –2 µA for 30, 4, and 100 seconds, respectively: (a) SEM micrograph, and EDX spectrums at the (b) top and (c) bottom ends.
Figure 5-18. TEM bright field images of two parts of nanowire plated with AAO template in Bath 3, at –60 µA, -7 mA, and –2 µA for 30, 4, and 100 seconds, respectively.

As mentioned previously, the low current pulse was set at the limiting current in DC plating. Therefore, the actually Cu plating rate, or the layer thickness, is expected not to deviate from the DC calculation. In contrast, the Co layer was found to be much smaller than the estimated value from DC plating. The deviation in Co layer thickness is believed predominantly
due to the transient effect in proton reduction. In spite of an increased pH, the proton reduction is much higher in high current pulse than the DC plating case, as a characteristic of pulse plating. Due to the long diffusion distance, the transient effect is much more severe than the case in thin film plating, which was carried out on rotating disk electrode.

5.4 Summary

A concentrated electrolyte was developed for the electrodeposition of FeCoNiCu alloy nanowires with AAO as template. The side reaction was successfully minimized in Cu nanowire plating by using a low potential. Co-rich alloy nanowires were plated at high potential, and an anisotropy in magnetization was observed, with an easy axis along the wire.

In double potential pulse plating, a significant deviation from DC plating was observed in the Cu layer. An anodic dissolution was also observed at the beginning of Cu plating pulse, resulting in a much thinner Co-rich alloy than DC plating. This dissolution was also observed at the relaxation pulse in triple potential pulses. With a galvanostatic pulse having a long relaxation period, nanowires of nanometric multilayers were fabricated successfully. The layer thickness deviated from the DC plating, consistent with the transient effect also observed in multilayer thin film plating.

5.5 References


6.1 Introduction

Compression molding has been used widely for decades to produce features with sizes larger than 1 µm, such as in compact disks. Recently nanoimprinting has been demonstrated to expand the molding technique for the fabrication of nanostructures.\textsuperscript{[1-3]} The advantage of imprint lithography lies in the cost-efficiency, and high throughput. Studies have shown the applicability of the imprinting process for fabrication of features with dimension in the 10 nm scale with electron beam lithography.\textsuperscript{[4-7]} Electron beam lithography, however, restricts the obtainable resolution due to limitations inherent in wave diffraction, scattering, and backscattering on the substrate.

Application of the nanoimprinting process has been focused on the fabrication of grating structures for optical or communication devices. For example, low refractive index passive optical devices were nanoimprinted with PMMA (polymethylmethacrylate) and PS (polystyrene).\textsuperscript{[8]} The mold was fabricated with a UV lithography process, and the duplicated grating structures were demonstrated to produce diffraction patterns with good resolution. Wang \textit{et al.}\textsuperscript{[9]} used nanoimprinting lithography process and fabricated waveguide polarizer with 190 nm period grating structures from a period mold prepared with interference lithography. The fabrication process was simple and compatible with conventional device processing. Circular optical structures with 20 nm feature size were fabricated later by the same group using nanoimprinting.\textsuperscript{[6]}
The nanoimprinting process is of interest due to the advantage of high throughput and low cost; however, the preparation of the mold itself traditionally involves lithography processes, like electron beam lithography and x-ray lithography, which is costly. In this study, a different approach is taken. An electrochemical method, including electrodeposition and selective chemical etching, is used to prepare a one-dimensional grating mold on a sub-micron scale, without reliance on a lithographic step.

The electrodeposition of nanometric multilayers has been widely demonstrated, motivated by the interest in giant magnetoresistance (GMR), which refers to a significant change of electric resistance of the material in the presence of an external magnetic field.[10-16] A multilayer refers to a layered structure with alternatively modulated distinct compositions. Due to the different composition of the alternating layers, it is possible to etch one of the two layers with the other intact. In this chapter, the established conditions for producing electrodeposited multilayers were expanded to yield nanomolds.

In Chapter III the FeCoNiCu/Cu multilayer was fabricated for the GMR property and the layer structure was verified with microscopic techniques.[17] Originated from the chemical property contrast of Cu and Co-rich FeCoNiCu alloy, the layered structure itself can be used to develop a grating structure by selectively etching one of the two layers. While the GMR requires the layer thickness of a few nm, in this chapter, multilayers with layer thickness on the order of 100 nm are fabricated for SEM (scanning electron microscope) investigation of the selective etching for mold development.

Prior research on Ni/Cu and Co/Cu multilayers,[18,19] have demonstrated selective etching of copper to provide contrast for SEM imaging. Bonhôte et al.[18] used a chromic acid solution to selectively etch the Cu layer in Ni/Cu multilayers for the examination of the structure with SEM.
A nitric acid alcohol solution was used for the same purpose by Bradley and Landolt for the Co/Cu system.\cite{19} This paper explores the use of the same technique for producing a nanostamp.

In multilayers of alloys, the selectivity of the etching solution changes. Furthermore, the selectivity is much more important than in the imaging case, since the quality of the structure developed is of interest. Also, the etching time becomes critical as well, and needs to be investigated. However, so far, no information of the etching time and quality has been available for multilayer systems.

In this chapter, the selective etching of FeCoNiCu/Cu nanometric multilayers was studied, as a potential tool for fabrication of nanoimprinting molds. The studies were restricted to multilayers with layer size from 100 nm to 1 \( \mu \)m, so that the analysis of the layer structure could still be carried out with SEM.

### 6.2 Experimental

The experimental setup and electrodeposition processes were described previously (see Chapter II). A sulfate electrolyte with additives was used for electrodeposition of alloy thin films and multilayers. Metal ion concentrations were, 8 mM FeSO\(_4\), 50 mM CoSO\(_4\), 57 mM NiSO\(_4\), and 1 mM CuSO\(_4\). Sodium potassium tartrate (27 mM), sulfamic acid (10 mM), sodium saccharin (4 mM) and triton X-100 (0.6 g/L) were present as additives.

Deposition was carried out on a stainless steel rotating disk electrode (RDE), on which a gold layer was plated, at 1000 rpm. The alloy deposit composition was studied previously as a function of the applied deposition current densities.\cite{17} The three DC-plated alloy used in this study were: Fe\(_{1}\)Co\(_{5}\)Ni\(_{3}\)Cu\(_{91}\) deposited at –3.54 mA/cm\(^2\); Fe\(_{15}\)Co\(_{73}\)Ni\(_{5}\)Cu\(_{7}\) deposited at –35.4 mA/cm\(^2\); and Fe\(_{13}\)Co\(_{71}\)Ni\(_{13}\)Cu\(_{3}\) deposited at –70.7 mA/cm\(^2\).
Stripping polarization curves were measured on the RDE at 2000 rpm, with a PC-controlled Pine bi-potentiostat, and the potential was corrected for the ohmic drop, which was measured by impedance analysis with a Bas-Zahner IM6 impedance measurement unit. Multilayers were pulse plated with an Amel potentiostat together with a Waveteck function generator. Microstructures developed after etching was examined with a JEOL JSM-840A scanning electron microscope (SEM), operated at 20 kV.

The preparation for most SEM samples includes cross sectional cutting, epoxy resin mounting, grounding and polishing, followed by selective etching. A 20-nm layer of gold was sputtered before secondary electron imaging. In another procedure of SEM sample preparation, the multilayer deposit was peeled off from the substrate, and was glued between two silicon pieces with Micro-Measurement M-Bond 600/610 curing agent before polishing and etching. This procedure doesn’t involve the epoxy and gold sputtering, and thus allows the use of organic solvent and direct examination with SEM.

Three etching strategies were examined in this study. The first one followed the study of Bradley and Landolt. The polished cross sectional sample was etched for 10 seconds in a dilute chromic acid solution containing 0.036 M H\textsubscript{2}SO\textsubscript{4}, 0.0034 M K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}, and 0.0012 M HCl, followed by a nitric acid alcohol solution, which was prepared by mixing 65% HNO\textsubscript{3} with ethanol by volumetric ratio 1:20. The action of the dilute chromic acid was reported to etch both layers uniformly to expose the sample. The HNO\textsubscript{3}/alcohol solution was responsible for the selective etching of Cu. The second solution was a concentrate K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} solution, used by Bonhôte et al. to selectively etch Cu in Ni-Cu multilayers. This K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} solution contained 0.034 M K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}, 0.36 M H\textsubscript{2}SO\textsubscript{4}, and 0.012 M HCl. The third solution used was an acidic ferric chloride-hydrochloric acid solution prepared by mixing 10 g FeCl\textsubscript{3}, 25 ml HCl (36 wt%) and 100
ml H₂O. This solution was adapted from Pace Technologies recommendation,[20] and usually used in industry for etching Cu and Cu alloys. Different from the first solution, etching in the later two solutions was a one-step process.

A demonstrative molding process was performed with STRUERS RepliSet-F5 silicon rubber. The fluid compounds were cast on the surface of the grating structure, and cured for 18 minutes. A 30 nm thick layer of Au was sputtered on the rubber before SEM examination. SEM examination was performed on the rubber structure at a lower voltage, 15 kV.

6.3 Results and Discussion

Before selective etching was applied to multilayers, investigations of different etching solutions were carried out with thin films deposited on RDE. Figure 6-1 shows polarization curves of different alloy deposits in three solutions. Alloy thin films previously deposited at three different current densities were used for corrosion analysis. Because the Cu rich thin film deposited at –3.54 mA/cm² oxidizes quickly in FeCl₃/HCl solution, bulk Cu was used instead. All the polarization curves follow Butler-Volmer behavior.

![Figure 6-1](image-url)

**Figure 6-1.** Polarization curves of bulk Cu (×) and alloy thin films deposited at –3.54 mA/cm² (+), -35.4 mA/cm² (○), and –70.7 mA/cm² (▲) in (a) HNO₃/alcohol solution; (b) concentrate K₂Cr₂O₇ solution; and (c) FeCl₃/HCl solution.
Linear extrapolation was used to obtain the corrosion potentials and current densities, which are presented in Tables 6-1 and 6-2. In HNO$_3$/alcohol solution, the corrosion current densities of the three alloy deposits are relatively low and close to each other. However, the difference in corrosion potentials is significant for the three alloys. Therefore, the less noble metal will be prone to corrosion. Contrarily, the corrosion potentials in FeCl$_3$/HCl solution are very close for different alloys while the corrosion current densities are obviously different. In this case, all the alloys corrode but at different rates. For K$_2$Cr$_2$O$_7$ solution, the difference in both corrosion potentials and currents for the three alloys are between the two previous cases. Generally, the corrosion rate in HNO$_3$/alcohol is much slower than the other two. From the
above discussion, the three solutions are all expected to show etching selectivity, because of the
difference of either the corrosion potentials (thermodynamics) or the corrosion currents
(kinetics).

**Table 6-1.** Corrosion current densities, $i_{\text{corr}}$ (mA/cm$^2$), for different deposits in different etching
solutions.

<table>
<thead>
<tr>
<th>deposit conditions</th>
<th>-3.54 mA/cm$^2$</th>
<th>-35.4 mA/cm$^2$</th>
<th>-70.7 mA/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$/alcohol</td>
<td>0.6</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Concentrate K$_2$Cr$_2$O$_7$</td>
<td>10.5</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>FeCl$_3$/HCl</td>
<td>10 (bulk Cu)</td>
<td>11</td>
<td>28</td>
</tr>
</tbody>
</table>

**Table 6-2.** Corrosion potentials, $E_{\text{corr}}$ (mV versus SCE), for different deposits in different etching
solutions.

<table>
<thead>
<tr>
<th>deposit conditions</th>
<th>-3.54 mA/cm$^2$</th>
<th>-35.4 mA/cm$^2$</th>
<th>-70.7 mA/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$/alcohol</td>
<td>125</td>
<td>4</td>
<td>-62</td>
</tr>
<tr>
<td>Concentrate K$_2$Cr$_2$O$_7$</td>
<td>50</td>
<td>-68</td>
<td>-80</td>
</tr>
<tr>
<td>FeCl$_3$/HCl</td>
<td>-148 (bulk Cu)</td>
<td>-138</td>
<td>-143</td>
</tr>
</tbody>
</table>

Based on the previous study, selective etching of FeCoNiCu/Cu multilayer structures on
micrometer scale was carried out. The thickness of the Co-rich layer was much larger than the
Cu-rich layer, in order to ease the determination of which layer is selectively etched. The SEM
pictures are presented in Figure 6-2.

Firstly, the Co-rich alloy was selectively etched in all cases, despite the fact that these
solutions are mostly used for selective etching of Cu in Ni/Cu and Co/Cu systems.$^{[18,19]}$ This
observation is believed to be ascribed to the presence of Fe in the Co-rich alloy, which is less
corrosion resistant. Considering the forgoing polarization studies, the underlying reason for the
selective etching of Co-rich alloy is different in these solutions. In HNO$_3$/alcohol and K$_2$Cr$_2$O$_7$,
the relatively positive corrosion potential for Cu makes it less prone to dissolve, and in the
FeCl$_3$/HCl, the higher corrosion current of Co-rich alloy determines it to be etched favorably. Secondly, the corrosion was more severe in the K$_2$Cr$_2$O$_7$ solution and FeCl$_3$/HCl solution despite the shorter etching time; and the low corrosion rate in HNO$_3$/alcohol was confirmed again.

![SEM micrographs](image)

**Figure 6-2.** SEM micrographs of (a) [FeCoNiCu]$_{1000}$ nm / Cu$_{100}$ nm after etching in HNO$_3$/alcohol for 4 minutes; (b) [FeCoNiCu]$_{2000}$ nm / Cu$_{500}$ nm after etching in concentrate K$_2$Cr$_2$O$_7$ solution for 1 minute; and (c) [FeCoNiCu]$_{2000}$ nm / Cu$_{500}$ nm after etching in FeCl$_3$/HCl solution for 1 minute, with layer thickness from theoretical calculation.
A comparison of the three micrographs, Figures 6-2 (a) to (c), shows that the selectivity of the K$_2$Cr$_2$O$_7$ solution is not as good as the other two. Polarization studies in Figure 6-1 (c) showed that the corrosion potential in this solution is considerably more positive for Cu-rich alloy than Co-rich alloy, resulting in the selective etching for the latter in terms of corrosion potential. But on the other hand, the higher corrosion current for the Cu-rich alloy favors the etching of Cu, and therefore the selectivity is deteriorated. The following studies for etching on multilayers with smaller dimensions excluded the concentrate K$_2$Cr$_2$O$_7$ solution.

Because the wavelength of optical light is of a few hundred nanometers, selective etching was studied for multilayers with submicron layer thickness. Figure 6-3 presents the structure developed with FeCl$_3$/HCl etching solution, from a multilayer with thickness on the order of 100 nanometers. From the micrograph, the Co-rich alloy layer thickness was found to be 130 nm and Cu layer was 200 nm, without considering the Au layer sputtered for imaging purposes. A high etching rate was observed, and the remaining Cu layer shows severe corrosion for an etching time of 2 minutes.
Figure 6-3. SEM (a) micrograph and (b) the enlarged graph of [FeCoNiCu]$_{130 \text{ nm}}$ / Cu$_{200 \text{ nm}}$ after etching in FeCl$_3$/HCl solution for 2 minute.

Further study was performed on multilayers with thinner layers with decreased etching times. The results are shown in Figure 6-4. Estimated from the enlarged micrograph insert, the two samples have sublayer thicknesses smaller than 100 nm, [FeCoNiCu]$_{80 \text{ nm}}$ / Cu$_{70 \text{ nm}}$ and [FeCoNiCu]$_{90 \text{ nm}}$ / Cu$_{90 \text{ nm}}$, respectively. The etching of the Cu layer was observed as well, which makes the layer thickness varying along the layer axis. More importantly, the poor alignment of the remaining Cu layer restricts the application of the structure to mold for optical grating.
Figure 6-4. SEM micrographs of (a) [FeCoNiCu]_{80\,nm} / Cu_{70\,nm} after etching in FeCl_3/HCl solution for 80 seconds and (b) [FeCoNiCu]_{90\,nm} / Cu_{90\,nm} after etching in FeCl_3/HCl solution for 50 seconds. The inserts are the respective enlarged micrographs.

The HNO_3/alcohol was investigated for the advantage of the slow corrosion rate. In Figures 6-5 (a) and (b), two etched multilayer samples are presented. The layer thicknesses derived from the image are [FeCoNiCu]_{170nm} / Cu_{300nm} and [FeCoNiCu]_{170nm} / Cu_{150nm}, respectively. The etching time was the same for the two samples, 2 minutes, and corrosion of the
Cu layer was not observed. The Co-rich alloy layer with a less positive corrosion potential was selectively etched, resulting in a good alignment and uniform etching. In Figure 6-5(c), a multilayer identical to the one in Figure 4 (a) is presented after etching. Due to the slow etch rate and the small dimension, the 9-minute etching was not sufficient and the nanostructure was not fully developed.

**Figure 6-5.** SEM micrographs of multilayers etched in HNO$_3$/alcohol: (a) [FeCoNiCu]$_{170\text{ nm}}$/Cu$_{300}$ for 2 minutes; (b) [FeCoNiCu]$_{170\text{ nm}}$/Cu$_{150\text{ nm}}$ for 2 minutes; and (c) [FeCoNiCu]$_{80\text{ nm}}$/Cu$_{70\text{ nm}}$ etched in HNO$_3$/alcohol for 9 minutes.
In addition to the extremely long etching time required for small dimensional multilayers due to the slow etching rate, the HNO$_3$/alcohol solution dissolves the mounting epoxy resin because of the organic solvent, alcohol. This usually causes fatal problems by covering the nanostructure developed during the etching procedure. It also prohibits the etching time from being long, which is usually required for samples of smaller dimensions. A procedure used for the cross sectional transmission electron microscope (TEM) sample preparation was adopted to get around this problem (see Experimental). Figure 6-6 shows micrographs of a [FeCoNiCu]$_{380\text{nm}}$/Cu$_{380\text{nm}}$ multilayer sample prepared with this procedure. Because the epoxy was avoided, the nanostructure developed in selective etching was completely exposed, and the SEM examination can be done directly to the sample without a gold layer for conductivity purpose. This procedure shows better candidacy for preparation of imprinting molds.

Another way to get around the epoxy problem is using an aqueous etching solution with a low corrosion rate. Other aqueous solutions, like NH$_3$/H$_2$O$_2$,$^{[20]}$ NH$_3$/H$_2$O$_2$,$^{[20]}$ and H$_2$SO$_4$/H$_2$O$_2$,$^{[21]}$ were also studied. The first two show a slow dissolution rate and fairly poor selectivity, and the
third one didn’t exhibit any selectivity. Among the solutions studied, only the FeCl₃/HCl and K₂Cr₂O₇ solutions were found good for selective etching of this multilayer system, with however too high corrosion rates. High corrosion rate requires short etch times, which makes it difficult to control. Polarization studies were carried out for a series of diluted solutions, and are shown in Figure 6-7 with the corrosion potentials and current densities listed in Tables 6-3 and 6-4.
Figure 6-7. Polarization curves of bulk Cu (+, ×, *) and alloy thin films deposited at -70.7 mA/cm$^2$ (▲, ♦) in (a) K$_2$Cr$_2$O$_7$ solution and (b) FeCl$_3$/HCl solution with no dilution (+, ▲), ½ dilution (×), and ¼ dilution (*, ♦).

Table 6-3. Corrosion current densities, $i_{corr}$ (mA/cm$^2$), and corrosion potentials, $E_{corr}$ (mV versus SCE), for Cu and Co-rich alloy in FeCl$_3$/HCl solutions with different dilution.

<table>
<thead>
<tr>
<th></th>
<th>bulk Cu</th>
<th>deposit at -70.7 mA/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$i_{corr}$ (mA/cm$^2$)</td>
<td>$E_{corr}$ (mV)</td>
</tr>
<tr>
<td>Concentrated</td>
<td>10</td>
<td>-148</td>
</tr>
<tr>
<td>½ diluted</td>
<td>20</td>
<td>-105</td>
</tr>
<tr>
<td>¼ diluted</td>
<td>15</td>
<td>-83</td>
</tr>
</tbody>
</table>
Table 6-4. Corrosion current densities, $i_{\text{corr}}$ (mA/cm$^2$), and corrosion potentials, $E_{\text{corr}}$ (mV versus SCE), for Cu and Co-rich alloy in K$_2$Cr$_2$O$_7$ solutions with different dilution.

<table>
<thead>
<tr>
<th></th>
<th>bulk Cu</th>
<th>deposit at -70.7 mA/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$i_{\text{corr}}$ (mA/cm$^2$)</td>
<td>$E_{\text{corr}}$ (mV)</td>
</tr>
<tr>
<td>Concentrated</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>½ diluted</td>
<td>22</td>
<td>30</td>
</tr>
<tr>
<td>¼ diluted</td>
<td>5</td>
<td>43</td>
</tr>
</tbody>
</table>

In FeCl$_3$/HCl solutions, either concentrated or four-fold volumetrically (¼) diluted, Cu is always more corrosion resistant than the Co-rich alloy. The difference of the corrosion potential is even larger in the diluted solution. However the corrosion current for Cu becomes higher than the Co-rich alloy, which favors the etching of Cu and thus makes the selectivity deteriorate.

In concentrated K$_2$Cr$_2$O$_7$ solution, the corrosion rate for bulk Cu is much higher than the Cu-rich alloy deposited at –3.54 mA/cm$^2$ (see Table 6-1), which includes tiny amount of iron-group metals, consistent with its corrosion selectivity of Cu over Ni.$^{[18]}$ In the ¼ diluted K$_2$Cr$_2$O$_7$ solutions, the corrosion rates were decreased significantly for both the Cu and Co-rich alloy, and the decrement for Cu is more significant than the Co-rich alloy, favoring the selective etching of the Co-rich alloy, opposite to the concentrated solution case. Therefore, the relative ease of Co-rich alloy corrosion is improved with the effects from corrosion potentials and currents becoming consistent and reinforcing each other.

Figures 6-8 (a) and (b) show the SEM images of two multilayers, [FeCoNiCu]$_{2000 \text{ nm}}$ / Cu$_{500 \text{ nm}}$ and [FeCoNiCu]$_{400 \text{ nm}}$ / Cu$_{200 \text{ nm}}$, respectively, after selective etching with the ¼ diluted K$_2$Cr$_2$O$_7$ solution. Although the layer thickness estimated from the enlarged micrograph inserts deviated from the theoretical calculation, as [FeCoNiCu]$_{1200 \text{ nm}}$ / Cu$_{500 \text{ nm}}$ and [FeCoNiCu]$_{300 \text{ nm}}$ / Cu$_{200 \text{ nm}}$, respectively, the effect of the dilution was obvious. In the diluted solution, the etching...
time is much longer compared with the concentrated solution case (see Figure 6-2 b), and the quality of the structure is considerably improved. The avoidance of the organic solvent allows the applicability to small dimensional features, and a uniform structure is observed throughout the whole millimetric range of the sample.

The molding process was carried out with silicon rubber at ambient conditions. The mold was developed by etching a micron size multilayer in the dilute K$_2$Cr$_2$O$_7$ solution for 3 minutes. Figure 6-9 shows the SEM micrographs of a duplicated grating structure, with the grating size

![Figure 6-8](image)

**Figure 6-8.** SEM micrographs of the multilayers after selective etching with $\frac{1}{4}$ diluted K$_2$Cr$_2$O$_7$ solution: (a) [FeCoNiCu]$_{1200}$ nm / Cu$_{500}$ nm for 2 minute, and (b) [FeCoNiCu]$_{300}$ nm / Cu$_{200}$ nm for 3 minute.
estimated as $1.5 \mu m$. The grating structure was easily duplicated in large area, as shown in Figure 6-9 (a). The quality of the structure was not as good as the mold, due to not only the molding process itself, but also to the preparation method of the molded piece for SEM investigation. Capillary force was the only driving force for the rubber to seep into the multilayered grooves. No vacuum was used, and residual air is believed to be present in the groove structure in the mold. Additionally, the rubber fluid compound was thick and cured fast, with a working life of 5 min. Therefore the fluid may not have completely seeped into the mold grating structure, resulting in a thin convex part. In addition, some bridged structures were observed, which is believed to result from the high temperature in the Au sputtering process, which can melt the rubber.

### 6.4 Summary

One-dimensional nanostructures for imprinting molds were developed by selective etching of FeCoNiCu/Cu multilayers. The Co-rich alloy was found to be selectively etched, opposite to most cases of Ni/Cu systems where Ni is the one that sustains etching. The selective

![Figure 6-9](image.png)

**Figure 6-9.** SEM micrograph of a duplicated micron-size grating structure on silicon rubber at (a) low and (b) high magnifications.
etching of the Co-rich alloy over Cu was mainly attributed to the less positive corrosion potential in HNO$_3$/alcohol and concentrate K$_2$Cr$_2$O$_7$ solutions, while in the FeCl$_3$/HCl case the higher corrosion current density was responsible for the selective etching. A SEM sample preparation procedure was developed to get around the problem of the incompatible organic solvent with the substrate holder in HNO$_3$/alcohol solutions. The dilution of the K$_2$Cr$_2$O$_7$ solutions was found to improve the selectivity of Co-rich alloy over Cu. A cast molding process was demonstrated at ambient conditions, and the grating structure was easily duplicated with silicon rubber.

6.5 Reference


CHAPTER VII. CONCLUSIONS

The electrodeposition of the FeCoNiCu quaternary system was studied, taking theoretical and experimental approaches. The electrochemical system was characterized by comparing with the FeNiCu alloy and pure elemental reduction behavior. Anomalous codeposition was observed in alloy systems, with deposition deviating from the order of nobility, Ni>Co>Fe. The deposition rate of Fe is enhanced, and Ni is inhibited. The plating of Co is inhibited before the Fe deposition becomes mass transport controlled, after which an enhancement of Co was observed. These observations are consistent with binary and ternary iron-group reduction behavior. The presence of Cu does not change the plating of the iron-group elements, however, the deposition rate of Cu is inhibited in the kinetic region.

With pulse plating, compositional modulated multilayers of FeCoNiCu/Cu were fabricated. Cu and Co-rich alloys were plated at low and high current densities, respectively. When the multilayer alloy thickness was larger than 10 nm, the deposit grain size was found to be a function of the Co-rich layer thickness. Below an alloy thickness of 10 nm, the Cu layer size was correlated with a preferred deposit orientation. GMR was also observed for this electrodeposited quaternary system for the first time, and a maximum value was correlated to when there is no preferred crystalline phases.

A series of FeCoNiCu/Cu multilayers with Cu layer thickness varying from 1.0 to 2.5 nm at a fixed alloy layer thickness of 2.0 nm was electrodeposited. A single maximum GMR occurred at a copper layer thickness of 1.8 nm, which corresponds to the second maximum peak reported for similar multilayers fabricated by vapor deposition. But the oscillatory behavior was not observed for these electrodeposited multilayers, probably due to the increased roughness at
layer interfaces resulting from the inherent characteristics of pulse electrodeposition. The saturation magnetic field was considerably larger than the vapor deposited counterparts. GMR of multilayers having a thicker alloy layer were sensitive to the magnetic field history, indicating the onset of anisotropic magnetoresistance. In addition, multilayers were also plated on polycrystalline Cu foil without agitation. Significantly improved GMR was observed, however with a higher response magnetic field.

A transient model was developed to describe the electrodeposition of FeCoNiCu/Cu nanometric multilayers onto a RDE, in both steady state and pulsed deposition cases. It includes a two-step adsorption mechanism for the description of anomalous codeposition, convective-diffusion mass transport and a displacement mechanism for pulses to zero current. Kinetic constants were obtained by fitting model simulation to experimental results in steady state cases. Changes in deposit composition were predicted with various pulse times as a tool for assessing interfacial compositional gradients in multilayer deposits.

Electrodeposition of the FeCoNiCu alloy system was also studied for the fabrication of nanowires. With anodic aluminum oxide membranes as a template, both Cu and Co-rich alloy nanowires were fabricated with potentiostatic methods. A lower potential was necessary to decrease side reactions and iron-group metal reduction during Cu nanowire plating. Magnetic anisotropy was observed for Co-rich alloy nanowires with an easy axis along the wire axis. A nanowire of 1.8 nm Cu / 4 nm FeCoNiCu multilayer was fabricated with a galvanostatic pulse scheme for the first time. The Cu layer size was found to be consistent with DC plating when being plated at a limiting current. A significant deviation of the layer size from DC plating was observed in Co-rich alloy layer, as expected for the transient effect in galvanostatic pulses.
Selective etching of FeCoNiCu/Cu multilayers was investigated for the development of nanoimprinting molds with different etching solutions, HNO$_3$/alcohol, FeCl$_3$/HCl and K$_2$Cr$_2$O$_7$/H$_2$SO$_4$. For all three solutions, the Co-rich alloy was found to be selectively etched, due to either a less positive corrosion potential or a higher corrosion current density than the Cu-rich layer. A better quality of a relief structure on the submicron layer size was dependent on a relative slow corrosion rate in etching solutions, making the etching easy to control. A dilute K$_2$Cr$_2$O$_7$ solution is considered most promising for submicron structure development, and a micron size grating structure was duplicated with cast molding process as a demonstration of the application.

As a general example of an alloy system composed of magnetic iron-group elements and a nonmagnetic element, the FeCoNiCu quaternary system was studied for electrodepositing different nanostructures. FeCoNiCu/Cu nanometric multilayers may find commercial interest in not only magnetic sensing and recording but also for nanoimprinting. The nanometric size of the layers can be well controlled by electrodeposition. As compared with vapor processes, electrodeposited multilayers have a less sharp interface in composition due to the inherent nonsteady state effect in pulse plating. However, it is the only method that satisfies all the temporal, financial and geometrical restrictions, making it a preferred method for nanowire fabrication and possibly nanoimprinting.
APPENDIX A. GOLD PLATING FOR STAINLESS STEEL DISK ELECTRODE

Stainless steel electrodes, 6 mm in diameter, were first mechanically polished with sand paper. Thereafter, the electrodes were cleaned with an ultrasonic cleaner and rinsed with double distilled water before Au plating.

The electrode surface was pretreated in a commercial Au strike solution for 10 min, with a current of −3.54 mA/cm² at rotation rate of 1600 rpm and 60 °C. Au was plated with a commercial solution, 0.25 E Au solution from Technic Inc., at a current density of −1.06 mA/cm², 1600 rpm and 60 °C for 12 min. The Au layer plated from this procedure is about 1 μm estimated from SEM image.
APPENDIX B. OHMIC DROP AND IMPEDANCE

The electrodeposition process can be approximately represented as a circuit with two resistors and a capacitor, illustrated in Figure B-1. The resistor, $R_{c.t.}$, represents the charge transfer resistance and the resistor, $R_{\Omega}$, represents the ohmic resistance. The capacitor represents the effect of the double layer capacitance that arises due to the charged species that approach or adsorb onto the electrode surface.

Impedance spectroscopy is a methodology where a series of small sinusoidal modulations of potential or current, with different frequencies, is applied. With the electrode system modeled as the circuit in Figure B-1, a typical impedance spectrum that would be expected is a semicircle in a Nyquest plot. A sketch of the Nyquest plot corresponding to the simple circuit is shown in Figure B-2. At very low frequency, the capacitor is equivalent to an open circuit and the impedance is equal to $R_{c.t.} + R_{\Omega}$. At very high frequency, the capacitor is equivalent to a short circuit and the impedance equals the ohmic resistance, $R_{\Omega}$. The ohmic resistance is then used to determine the ohmic drop ($I \cdot R_{\Omega}$) in the electrolyte: $E_{true} = E_{read} - I \cdot R_{\Omega}$.

![Figure B-1. Representation of electrodeposition process](image)

"Figure B-1. Representation of electrodeposition process"
Figure B-2. Typical Nyquist plot of impedance spectroscopy
APPENDIX C. TARTRATE-METAL COMPLEXATION

The effect of tartrate-metal ion complexation was determined by calculation based on stability constants from literature.\[1\] The algebraic equations used in calculation are as follows.

\[ C_{M_j^{2+}} + C_{M_jL} = C_{M_jSO_4} \quad \text{Eq. C-1} \]

\[ C_{L^{2-}} + C_{HL^-} + C_{H_2L} = C_{NaKL} \quad \text{Eq. C-2} \]

\[ C_{H^+} + C_{HL^-} + 2 \cdot C_{H_2L} = C_{\text{proton}} \quad \text{Eq. C-3} \]

where \( L^{2-} \) represents the ligand anion, \( NaKL \) is the sodium potassium tartrate, and \( C_{\text{proton}} \) is the total concentration of proton in solution. The concentration of free \( H^+ \) was fixed by adjusting the pH at 2.5. The relations between complexed and uncomplexed species are governed by stability constants,

\[ M_j^{2+} + L^{2-} \rightleftharpoons M_jL \quad \text{Eq. C-4} \]

\[ K_{s,j} = \frac{C_{M_jL}}{C_{M_j^{2+}} \cdot C_{L^{2-}}} \quad \text{Eq. C-5} \]

\[ H^+ + L^{2-} \rightleftharpoons HL^- \quad \text{Eq. C-6} \]

\[ K_1 = \frac{C_{HL^-}}{C_{H^+} \cdot C_{L^{2-}}} \quad \text{Eq. C-7} \]

\[ H^+ + HL^- \rightleftharpoons H_2L \quad \text{Eq. C-6} \]

\[ K_2 = \frac{C_{H_2L}}{C_{H^+} \cdot C_{HL^-}} \quad \text{Eq. C-7} \]
Figure C-1 shows the percentage of different uncomplexed cation species present in the solution as a function of pH, calculated from the complexing constants listed in Table C-1.\textsuperscript{[1]} At the pH of the electrolyte used in this study the dominant complexed species are Co(II) and H(I), and most other metal ions are present as free cations.

**Table C-1.** Stability constants for different metal cations and proton with tartrate\textsuperscript{[1]}

<table>
<thead>
<tr>
<th>cation species</th>
<th>Fe\textsuperscript{++}</th>
<th>Co\textsuperscript{++}</th>
<th>Ni\textsuperscript{++}</th>
<th>Cu\textsuperscript{++}</th>
<th>H\textsuperscript{+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK_s$</td>
<td>2.96</td>
<td>3.53</td>
<td>3.01</td>
<td>3.1</td>
<td>3.78 ($pK_1$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.73 ($pK_2$)</td>
</tr>
</tbody>
</table>

**Figure C-1:** Percentages of different cation species (Fe: ○; Co: ■; Ni: ●; Cu: +; H: □) present in the solution in an uncomplexed form as a function of pH.

**References**

### APPENDIX D. LIST OF SYMBOLS

- **A**: Surface area occupied by unit amount of adsorbed intermediate, $[cm^2 \cdot mol^{-1}]$
- **$a_j$**: Activity of species $j$, $[mol \cdot cm^{-3}]$
- **$a_j^*$**: Activity of species $j$ at electrode surface, $[mol \cdot cm^{-3}]$
- **$a_{M_2}$**: Activity of metal component, $M_2$, in alloy solid, $[mol \cdot cm^{-3}]$
- **$\alpha_c$**: Transfer coefficient for cathodic reaction
- **$b_k$**: Tafel slope of reaction $k$, $[V^{-1}]$
- **$C^b$**: Bulk concentration, $[mol \cdot cm^{-3}]$
- **$C^s$**: Surface concentration, $[mol \cdot cm^{-3}]$
- **$C_{H^+}$**: Concentration of free proton in solution, $[mol \cdot cm^{-3}]$
- **$C_{proton}$**: Concentration of all proton in solution, in complexed and free status, $[mol \cdot cm^{-3}]$
- **$C_{HL}$**: Concentration of the tartrate ligand complexed with one proton, $[mol \cdot cm^{-3}]$
- **$C_{H_2L}$**: Concentration of the tartrate ligand complexed with two protons, $[mol \cdot cm^{-3}]$
- **$C_{dl}$**: Double layer capacitance, $[F \cdot cm^{-2}]$
- **$C_j$**: Concentration of species $j$, $[mol \cdot cm^{-3}]$
- **$C_j^b$**: Bulk concentration of species $j$, $[mol \cdot cm^{-3}]$
- **$C_{L^{2-}}$**: Concentration of free tartrate ligand, $[mol \cdot cm^{-3}]$
- **$C_{M_j^{++}}$**: Concentration of cation, $M_j^{++}$, $[mol \cdot cm^{-3}]$
- **$C_{M_1^{++}}$**: Concentration of a more noble iron-group metal, $M_1^{++}$, $[mol \cdot cm^{-3}]$
- **$C_{M_2^{++}}$**: Concentration of a less noble iron-group metal, $M_2^{++}$, $[mol \cdot cm^{-3}]$
- **$C_{M^{n+}}$**: Surface concentration for metal ion species, $M^{n+}$, $[mol \cdot cm^{-3}]$
- **$C_{M_jLM}$**: Concentration of complexed cation, $M_j^{++}$, in a form of $ML$, $[mol \cdot cm^{-3}]$
\( C_{M,SO_4} \) Total concentration of cation, \( M^{++} \), as sulfate, [\( mol \cdot cm^{-3} \)]

\( C_{NaKL} \) Total concentration of all tartrate ligand, [\( mol \cdot cm^{-3} \)]

\( C_{O_2} \) Concentration of oxygen in solution, [\( mol \cdot cm^{-3} \)]

\( C_{O_2}^b \) Bulk concentration of oxygen in solution, [\( mol \cdot cm^{-3} \)]

\( d \) Thickness of deposit, [\( cm \)]

\( d_{grad} \) Thickness of transient region, [\( nm \)]

\( D_j \) Diffusion coefficient of species \( j \), [\( cm^2 \cdot s^{-1} \)]

\( D_{O_2} \) Diffusion coefficient oxygen in solution, [\( cm^2 \cdot s^{-1} \)]

\( \delta_{N,j} \) Diffusion boundary layer for species \( j \), [\( cm \)]

\( \delta_{O_2} \) Diffusion boundary thickness of oxygen, [\( cm \)]

\( E \) Potential, [\( V \)]

\( E^0 \) Standard potential, [\( V \)]

\( E_{rev} \) Reversible potential, [\( V \)]

\( F \) Faraday’s constant, 96485 [\( coulomb \cdot equiv^{-1} \)]

\( i_c \) Current density of cathodic reaction, [\( mA \cdot cm^{-2} \)]

\( i_0 \) Exchange current, [\( mA \cdot cm^{-2} \)]

\( i_{lim,O_2} \) Limiting current density of the reduction of oxygen, [\( mA \cdot cm^{-2} \)]

\( i_{total} \) Total current density applied, [\( mA \cdot cm^{-2} \)]

\( \eta \) Overpotential, [\( V \)]

\( j \) Subscript for species number

\( k_c \) Rate constant of a cathodic reaction, various units

\( k_{c,0} \) Rate constant of a cathodic reaction at zero potential, various units

\( k \) Subscript for reaction number

\( k_k, k_{-k} \) Rate constant of reaction \( k \) in cathodic and anodic direction, various units.

\( k_k^0 \) Reaction constant at zero potential for reaction, \( k \), various units.
\[ MW_j \] Molecular weight of metal species \( j \), \( g \cdot mol^{-1} \)

\( n \) Number of electron involved in a cathodic reaction

\( n_k \) Number of electron involved in reaction \( k \)

\( \nu \) Kinematic viscosity of solution, 0.01 \( cm^2 \cdot s^{-1} \)

\( p_M \) Reaction order in terms of reactant, \( M \)

\( \theta_{\text{empty}} \) Fraction of surface area which is unoccupied by any intermediate

\( \theta_j \) Fraction of surface area occupied by intermediate \( j \)

\( \theta_{H_{\text{ads}}} \) Fraction of surface area occupied by the intermediate, \( H_{\text{ads}} \)

\( \theta_{M_{j_{\text{ads}}}^{+}} \) Fraction of surface area occupied by the intermediate, \( M_{j_{\text{ads}}}^{+} \)

\( \theta_{[M_iM_j]_{\text{ads}}^{++}} \) Fraction of surface area occupied by the intermediate, \( [M_iM_j]_{\text{ads}}^{++} \)

\( R \) Gas constant

\( R_{\text{c.t.}} \) Charge transfer resistance, \( \Omega \)

\( R_{\Omega} \) Ohmic resistance, \( \Omega \)

\( r_c \) Reaction rate of a cathodic reaction, \( mol \cdot cm^{-2} \cdot s^{-1} \)

\( r_{j,1}, r_{j,2} \) Reaction rates of the first and second steps in metal reduction, \( mol \cdot cm^{-2} \cdot s^{-1} \)

\( r_k \) Reaction rate of reaction \( k \), \( mol \cdot cm^{-2} \cdot s^{-1} \)

\( \rho_j \) Density of metal species \( j \), \( g \cdot cm^{-3} \)

\( s_j \) Stoichiometric number of species \( j \)

\( s_{jk} \) Stoichiometric number of species \( j \) in reaction \( k \)

\( T \) Temperature, \( K \)

\( t \) Time, \( s \)

\( \Delta t \) Step of increment of time in calculation, \( s \)

\( u_x \) Velocity of liquid electrolyte in axial direction, \( cm \cdot s^{-1} \)

\( x \) Distance from electrode surface, \( cm \)

\( x_j \) Content of metal species \( j \) in alloy deposit, \( % \)

\( V \) Applied potential, \( V \)

\( \omega \) Angular velocity of rotating disk electrode, \( rad \cdot s^{-1} \)
APPENDIX E. LETTERS OF PERMISSION

Terry McCloughan

From: Giang Huang [qhuang1@lsu.edu]
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Sincerely,

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If you have further questions please don't hesitate to call me at (225) 578-4687 or (225) 892-7305. Thank you for your considerations.

Sincerely

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http://mail181.lsu.edu/mail18f/qhuang1.nsf/38d46bf5e8f08834852564b500... 11/12/2003
Mr. Qiang Huang was born in Suzhou, China in the spring of 1775. He was enrolled in Zhejiang University in 1993, for a Bachelor’s program in chemical engineering. Upon the completion in 1997, he worked as a teacher in Suzhou No.3 Middle School for one year, followed by one year as an engineer in Chung-Hwa Chemicals & Pharmacies, Inc. In 1999 August, he went to Louisiana State University and has been working toward a doctoral degree in chemical engineering, which will be conferred in May 2004.