Electrodeposition of magnetic nanowires and nanotubes

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ELECTRODEPOSITION OF MAGNETIC NANOWIRES AND NANOTUBES

A Thesis

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
Master of Science

in

The Department of Chemical Engineering

By
Despina Mehedintu Davis
B.S., Texas Tech University, 2002
May, 2005
To my parents
ACKNOWLEDGEMENTS

I would like to sincerely thank my advisor, Dr. E. J. Podlaha, for all her help, support and remarkable ideas that made this thesis work successful.

I thank Dr. A. B. Corripio and Dr. K. E. Thompson from LSU Chemical Engineering Department for accepting to be on my graduate committee.

For all the magnetic measurements support, I would like to thank Dr. M. Moldovan and Dr. D. P. Young from LSU Physics Department.

Dr. X. Xie in Geology Department and Ms. Henk in Life Science helped me gather nice sets of data and micrographs, for which I am very thankful.

I would like to thank my colleagues Dr. Q. Huang, Dr. J. Zhang, Mr. R. Mishra and Mr. Y. Li. for the helpful discussions.

National Science Foundation financially supported this project.
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ABSTRACT

The current perpendicular to the plane giant magneto-resistance (CPP)-(GMR) effect makes multilayered nanowires of huge interest as magnetic sensor materials. GMR showing multilayer nanostructures are composed of alternating ferromagnetic and nonmagnetic nanometric layers. The giant magnetoresistance (GMR) property is described as a change in electrical resistance when an external magnetic field is introduced.

Electrodeposition is the most efficient method for fabricating magnetic nanowires. In addition to the cost-effectiveness, electrodeposition is one of the few methods that can overcome the geometrical restrictions of inserting metals into very deep nanometric recesses, making it the favored method for nanowire and nanotube fabrication. In this thesis, the quaternary FeCoNiCu alloy system was investigated in order to electrodeposit multilayered nanowires/nanotubes for GMR effect. The choice of CoNiFeCu quaternary system allows the flexibility to optimize the magnetic property (GMR) by varying deposit composition.

This study demonstrates the ability to fabricate multilayered CoNi(Fe)Cu/Cu nanowires using different templates: polycarbonate membranes (PC) and porous alumina filters (AAO). Layer thicknesses were controlled and varied for commercially viable GMR results. The effect of electrolyte additives and concentration was demonstrated to have an effect on the GMR. Greater than 10 % GMR, at room temperature and at small magnetic fields (< 0.5 Tesla), is reported for the first time in CoNiCu/Cu and CoNiFeCu/Cu nanowires.

CoNiCu nanotubes in PC membranes were also fabricated for the first time. Conditions for electrodepositing multilayered nanotubes that exhibit GMR has been established and is a pioneering effort in the field.
CHAPTER I INTRODUCTION

1.1 Electrodeposition and Magnetic Materials

Technological applicability of metallic submicron structures has generated tremendous interest in recent years because of their potential. The discovery of giant magnetoresistance (GMR) in 1988 by Baibich et al. [Baibich, 1988] marked the beginning of an intense research topic. Manufactured materials that show GMR are used for perpendicular magnetic recording and magnetic field sensors. These magnetic materials make good candidates for computer disk drives, audio-video tape heads, magnetometers, compass systems, etc. Downsizing disk drives involves higher disk drive densities, which in turn requires very small read heads with better sensitivity to detect smaller bits and weaker magnetic fields. The goal is to obtain the largest change in resistance for small magnetic field variations. Currently, most magnetic drives read stored data using GMR-based heads. Based on its orientation, the small magnetic field of each magnetic particle on the disk affects the electrical resistance of the read head. When the magnetic layers of the head sense a magnetic moment signifying "1" the spins align, and when it senses a "0" the spins become anti-ferromagnetically coupled. In one position the electrical resistance is high, since the magnetic moments are not aligning, letting only a small current pass through the read head. On the other hand, the magnetic moment signifying “1” decreases the electrical resistance, letting a high current to pass though the head. The shifting strengths of an electrical signal, as a result of changes in electrical resistance, allow the GMR read head to copy stored data to a computer.

The GMR effect can also be used for position detection devices of objects that have permanent imprinted magnetization patterns. Robotics and assembly lines use position sensors that sense a change in magnetic field due to the movement of a magnetized object. GMR sensors
could be very small. Moreover, the CPP sensor performance can even improve upon miniaturization. GMR sensors possess higher sensitivity, better signal-to-noise ratios, and exhibit less mechanical wear since they could be considered contactless sensors.

The study proposed by Baibich et al. showed that an applied magnetic field changes the spin alignment of the ferromagnetic layer from antiparallel to parallel, resulting in a decrease of material resistance. According to Mott [Mott, 1964] electrical current is comprised of two distinct conduction channels, the spin-up and spin-down s-p electrons, and the conductivity is different in the two spin channels. When a perpendicular current is applied to a magnetic layer, the electrons with spin parallel to the magnetized layer (majority carriers) will be scattered less than the electrons with spin antiparallel to the magnetization layer (minority carriers). In the case of no applied magnetic field, the majority carriers are strongly scattered in every other magnetic layer, and the minority carriers are strongly scattered in the alternating every other magnetic layer, therefore both carriers encounter higher net resistance. When a magnetic field is applied to this configuration, the electrons in all the ferromagnetic layers will orientate such that the majority carriers are not strongly scattered in any of the magnetic layers. The minority carriers are still scattered in all of the magnetic layers, but the net effect of this rearrangement is a lower resistance to the current passing through the multilayered material.

Shortly after the first GMR demonstration, Binasch et al. [Binasch, 1989] reported that the antiparallel state of iron magnetization yields a larger magnetoresistance than the parallel state. This antiparallel state of magnetization at zero applied magnetic fields, which gives rise to GMR, is not to be confused with the anisotropic magnetoresistance (AMR), an effect described by McGuire and Potter [McGuire, 1975] which is related to spin-orbit scattering leading to a resistance sensitive to the angle between the current density and the magnetization in bulk ferromagnets.
Prior to 1990’s, vacuum sputtering, molecular beam epitaxy, melt spinning and ball milling were the only methods used to obtain multilayered films for GMR purposes. Vapor techniques showed large GMR values (70% at room temperature and 130% at 4.2 K) for thin Co/Cu multilayer films, Parkin [Parkin, 1995]. In the past ten years, electrodeposited GMR films have recently been examined as an alternative, less costly process.

Ross [Ross, 1994] reviewed electrodeposition as an alternative technique for making multilayer films, and pointed out that electrochemical methods permit the manipulation of mechanical properties and orientation dependent properties. However, lower GMR values have been reported for electrodeposited films. The reviewer mentioned that non-discrete layering, rough interfaces and heterogeneous growth could contribute to the lower values of GMR obtained by electrodeposition.

Even though there is room for much improvement, the low cost of investment and operation, in addition to high deposition rate, make electrodeposition a versatile method for coating and thin film manufacturing. Electrodeposition, however, finds a niche in assembling nanometric size structures in complex geometries and recessed areas. The vapor deposition techniques are of little value when it comes to inserting metals into very deep recesses, such as nanoporous membranes. Electrodeposition is the easiest and most practical way of obtaining nanowires, by inserting metals in porous membranes.

1.2 Goal of Research: Nanowires

Aside from the fact nanoscale materials exhibit different behavior compared to bulk materials, nanowires are structures of enormous surface area and aspect ratios (length to diameter), which confer them unique properties. Due to nanowire unique geometry, the GMR property can be measured in a perpendicular mode (CPP), which has been proven to show larger changes in electrical resistance with magnetic fields than the (CIP) GMR (in-plane)[Pratt, 1991].
Although various systems were tested for making multilayered nanowires using the electrodeposition method, the research is still in the incipient phase and needs further investigation. To the best of our knowledge, no examination of the combined Co-Ni-Fe-Cu system in nanowires has been done up to present. Therefore, the present work focuses on this quaternary CoNiFeCu/Cu electrodeposition in the form of multilayered nanowires using polycarbonate (PC) and aluminum oxide (AAO) membranes. The magnetic properties of the obtained nanowires were tested and related to changes in the electrodeposition operating conditions, such as applied potential and electrolyte composition.
CHAPTER II LITERATURE REVIEW

The GMR effect is dependent on the morphology, which can be altered by changes in electrodeposition conditions, such as electrolyte composition, applied current, deposition regime (mass transport or kinetic), and deposition techniques (potentiostatic/galvanostatic). The GMR is also a function of the magnetic and non-magnetic layer thickness, choice of substrate, and layers number.

2.1 Multilayered Nanowires

Focusing on thin film magnetic layers sandwiched with non-magnetic layers, Parkin [Parkin, 1995] reviewed the magnetoresistance dependence in layered structures. The reviewer emphasized the layered materials requirements in order to be used for magnetic data storage applications: magnetic stability against increased temperatures, no electromigration at high current density usage and minimal environmental corrosion. A decrease in GMR was observed when the alternating magnetic layers were not completely antiferromagnetically coupled, due to larger layer sizes or non-discrete layers. High GMR was exemplified for vapor deposition techniques, such as Co/Cu thin films obtained by magnetron sputtering had 70 % GMR at room temperature, 130 % GMR at 4.2 K, and 220 % GMR at 1.5 K.

Ross [Ross, 1994] also reviewed magnetic thin films but focused on the electrodeposition process as an affordable alternative method of obtaining multilayer thin films. The electrodeposition advantages highlighted the ability to tailor the deposit composition and crystallographic structure. Ross also pointed out that electrolyte composition, pH, agitation and current regime affect the multilayer fabrication process. The reviewer, called attention to the 18 % GMR at room temperature observed in the CoNiCu/Cu electrodeposited thin films. Aside from bath composition and deposition conditions, Ross mentioned that additives and the choice of substrates have an effect on the crystal nucleation and epitaxial growth.
In thin films, the GMR is measured with the electric current in plane of the multilayers, the so-called (CIP) configuration. The nanowire GMR is measured in current perpendicular to the plane of multilayers (CPP) configuration. The characteristic length is the feature that controls the GMR effect, and it differs in the two configurations, CIP and CPP. In the case of CIP (thin films), the electron mean free path is the characteristic length that dictates the GMR. In the CPP mode (nanowires), the spin diffusion is the characteristic length that governs the GMR. [Schawarzacher, 1996, Piraux, 1996] Valet and Fert (Valet, 1993) derived an expression which relates the electron mean free path (\( \ell _e \)) to the spin diffusion length (\( L \)). Since the electron mean free path (\( \ell _e \)) in CIP is about ~2 nm, the layer thicknesses in the CIP mode is critical. On the other hand, in the CPP configuration, the greater spin diffusion length ~ 20 nm allows for larger layer thickness. Piraux et al. (Piraux, 1994) showed that in the CPP configuration a sample of Co(10 nm)/Cu(10 nm) yielded 15% GMR at room temperature, which could also be achieved in the CIP mode, only that the Cu layers had to be a lot smaller (0.8 nm).

It is experimentally difficult to measure CPP-GMR in thin films due to their very small resistance, but arrays of nanowires make this configuration readily accessible. The CPP configuration is conducive for tall and narrow geometries such as nanowires. Piraux et al. (Piraux, 1994) was the first to take advantage of the multilayer nanowire geometry. They studied the Co/Cu system electrodeposited in polycarbonate membranes (PC) (40 nm pore diameter and 10 m pore length), and reported the CPP-GMR to be 15% at room temperature for (10 nm Co/10 nm Cu) layers.

Concurrently, Blondel et al. (Blondel, 1994) looked at the Co/Cu and FeNi/Cu multilayers electrodeposited in nanowires. Blondel et al. also measured CPP-GMR at room temperature, and obtained a slightly higher GMR (14 %) for the Co/Cu system than for the FeNi/Cu system (10 %). Using PC membranes (80 nm pore diameter and 6 m pore length),
Blondel et al. tested different layer thicknesses and found that a larger GMR was shown for layers less than 10 nm.

Liu et al. (Liu, 1995) retested the Co/Cu system for layers in nanowires, and found 11 % CPP-GMR at room temperature, and 22 % CPP-GMR at 5 K. Testing two different kinds of polycarbonate membranes (30 nm pore diameter/ 6 m pore length, 400 nm pore diameter /10 m pore length), Liu et al. utilized coulometric potential control electrodeposition as the method for fabricating nanowires. In the different CIP and CPP GMR measurements, they found that the nanowire CIP-GMR was temperature independent, while the CPP-GMR was especially sensitive to temperature. Testing different Cu layer thicknesses ranging from 8 to 400 Å, they observed that the GMR effect becomes insignificant for Cu layer thicknesses exceeding the spin-flip diffusion length. For Cu layer thicknesses of (0.8 nm), the CPP-GMR was reported to be 22 % at low temperatures. The GMR as a function of Cu layer thicknesses showed two separate peaks, but no clear values were given. Liu et al. concluded that the CPP-GMR effect in nanowires was due to the layered arrangement combined with an extra interfacial resistance. Furthermore, the smaller diameter wires showed significant boundary scattering that could explain the larger observed GMR.

Blondel et al. (Blondel, 1995) also studied the CPP-GMR in electrodeposited multilayered nanowires, using polycarbonate membranes (80 nm pore diameter/ 6 m pore length). Blondel et al. sandwiched CoNi/Cu using a square pulsed potentiostatic technique, and obtained very smooth and flat layers. For equal magnetic and nonmagnetic layer thicknesses, the measured CPP-GMR was 20 % at room temperature. Both the nonmagnetic impurity level and the strict interface control were presented as the key factors in maximizing the GMR property.

Wang et al. (Wang, 1996) prepared Ni/Cu multilayered nanowires using polycarbonate membranes (80 nm pores diameter/ 8 um pore length) as templates. Employing a potentiostatic
pulsed scheme, Wang et al. observed that the multilayers displayed a concave growth. A disagreement between the pore diameter and the wire diameter was observed, which was explained as wire expansion during electrodeposition. Wang et al. also reported that the bilayer thickness increased as the wire grew when a potentiostatic pulsed scheme was used.

To obtain pure layers nanowires, Blondel et al. (Blondel, 1997) implemented a dual bath technique electrodeposition, and then compared the results with the ones obtained from the single bath deposition. Analyzing the Co/Cu system and keeping both magnetic and nonmagnetic layer thicknesses the same, Blondel et al. reported 8 % GMR for 10 nm layers using the dual bath technique. On the other hand, Blondel et al. reported 22 % GMR for 8 nm layers obtained from the single bath electrodeposition. As a consequence, Blondel et al. concluded that the impurity of Cu in the Co layer, inherent in the single bath, was not the determining factor for the GMR effect.

Dubois et al. (Dubois, 1999) compared the NiFe/Cu system with the Co/Cu system for the CPP-GMR effect in PC membranes. At 77 K, the 10 nm Co/ 5 nm Cu multilayered nanowires showed 30 % GMR, and the 12 nm Ni$_{80}$Fe$_{20}$/ 4 nm Cu had 65 % GMR. At an even lower temperature (4.2 K), Dubois et al. saw an increase of the CPP-GMR to 78 % for the NiFe/Cu multilayers. They did not report room temperature GMR.

Simultaneously, both Schwarzacher et al. (Schwarzacher, 1997) and Heydon et al. (Heydon, 1997) researched a more complex combination of elements and were able to obtain multilayered CoNiCu/Cu nanowires in polycarbonate membranes. Schwarzacher et al. reported a maximum GMR of 22 % at room temperature for CoNiCu (50 Å)/ Cu (40 Å) multilayered nanowires in 80 nm pore diameter membrane. In the same study Schwarzacher et al. hypothesized that adding Ni to the bath reduced Co dissolution during the Cu deposition. In a later study, Huang and Podlaha (Huang, 2004) showed that Co dissolution during Cu deposition
could exaggerate the compositional gradient at the interface, making the layers less discrete.

Even for thicker layers (5 nm CoNiCu/3.5 nm Cu) Heydon et al. showed 20 % GMR at room temperature. When the Cu layer decreased (2.4 nm CoNiCu/3.5 nm Cu) the GMR increased to 22 % at room temperature.

Comparing a typical multilayer arrangement Ni$_{80}$Fe$_{20}$ (12 nm)/Cu (4 nm) and a trilayered layer arrangement Ni$_{80}$Fe$_{20}$ (3 nm)/Cu (10 nm)/ Ni$_{80}$Fe$_{20}$ (3 nm) separated by 90 nm long Cu fragments, Piraux et al. (Piraux, 1997) observed a decrease in magnetic saturation fields for the trilayered nanowires obtained in aluminum oxide templates. At low temperature (4.2 K) and high magnetic fields (9 T), 80 % CPP-GMR was obtained for the typical multilayered NiFe/Cu system, while a 19 % CIP-GMR, at low saturation fields, was observed for the trilayered nanowires. When the same GMR measurements were performed at room temperature, the MR decreased to a third (~ 26 %) of the low-temperature GMR value.

Evans et al. (Evans, 2000) investigated the electrodeposition of CoNiCu/Cu multilayers in 20 nm pore diameter aluminum oxide templates. Using potentiostatic charge control to control layer thicknesses, they reported 55 % room temperature GMR and 115 % low temperature GMR, for sub-nanometric layer sizes CoNiCu (54 Å)/Cu (21 Å). Evans et al. concluded that the GMR observed in the AAO membranes was 2.5 times larger than the GMR obtained for a comparable system deposited in PC membranes. Their study also showed that sample annealing over 500 °C would reduce the GMR effect due to interdiffusion and recrystallization phenomena.

Schwarzacher et al. (Schwarzacher, 2000) used 20 nm diameter pores AAO templates for electroplating multilayered nanowires. They pointed out that AAO pore size specification was an order of magnitude smaller than the observed pore diameter (200 nm). Using galvanostatic electrodeposition, Schwarzacher et al. achieved 60 % room temperature GMR for CoNiCu (5nm)/Cu (3nm) multilayered nanowires. Schwarzacher et al. concluded that the AAO
membranes were a better choice for electrodepositing nanowires than the polycarbonate membranes.

Garcia et al. (Garcia, 2002) showed that multilayered wires of extreme magnetic layer thickness, such as Co (170 nm)/Cu (10 nm) and Co (25 nm)/Cu (190 nm) exhibited inconsistent magnetic states, having transverse and oblique magnetic domains.

2.2 Single Component Nanowires

Ounadjela et al. (Ounadjela, 1997) studied the magnetic properties of Co nanowires electrodeposited in polymer membranes (PC) of various pore sizes and observed strong magneto-crystalline anisotropy perpendicular to the wire axis. Ounadjela et al. also pointed out that in small diameters nanowires Co acts as a single domain structure with the easy axis parallel to the nanowire axis.

Piraux et al. (Piraux, 1997) realized a comparative study of ferromagnetic Co, Ni, Fe nanowires grown by electrodeposition in polycarbonate membranes of various pore diameters, ranging from 30 to 500 nm. Using low porosity membranes for low dipolar interactions, the researchers observed that all Co, Ni and Fe nanowires exhibited an increase in coercivity as the pore diameter decreases. However, for Co and Ni nanowires, the remanent magnetization decreased with pore diameter, which suggests that wires split into domains when the pores were large. In the case of Co only nanowires, the shape anisotropy competed with the crystal anisotropy, which led to a specific magnetic behavior. Piraux et al. concluded that Ni and Fe nanowire magnetic properties were governed by the shape anisotropy.

Schwanbeck and Schmidt [Schwanbeck, 2000], using both porous aluminum templates and polycarbonate membranes, tested different electrolytes and examined the influence on the magnetic properties of Co nanowires. Initially, in the non-steady-state fraction of the electrodeposition, galvanostatic control was employed until the voltage reached a constant value
at which time the potential was controlled. The authors observed that the growth of nanowires inside the membrane stopped if some of the nanowires have reached the surface. The boric acid (pH 3.7) bath yielded the least coercive nanowires in comparison to the propionic acid (pH 6.7) and maleic acid (pH 6.8) baths. The nanowires obtained in AAO membranes of 200 nm pore diameter showed similar magnetic results in both perpendicular and in-plane measurements. The nanowires grown in PC membrane (100 nm pore diameter) showed higher coercivity for the in-plane measurements compared to the perpendicular to the wire axis measurements.

Interested in data recording materials, Ge et al. (Ge, 2000) studied the perpendicular magnetic anisotropy of high-density surface distribution Co nanowires electrodeposited in polycarbonate membranes. Using 400 nm pore diameters membranes, Ge et al. applied a magnetic field during the potentiostatic electrodeposition of the nanowires, and different results were obtained when the electrodeposition magnetic field was perpendicular or parallel to the membrane plane. Significant differences in the crystalline structures were observed as a function of magnetic field direction. When the magnetic field applied during the electrodeposition was perpendicular to the membrane, the magnetic anisotropy was enhanced. Furthermore, the perpendicular magnetic field led to a larger coercivity and improved squareness due to a preferred growth direction of the Co crystal under magnetic field influence. Ge et al. showed that the Co particles deposited in the pores would have random crystallographic orientation without an applied magnetic field that would force the cobalt grain axis along the applied magnetic field, resulting in a stronger structure.

Garcia et al. (Garcia, 1999) investigated the electrodeposition and magnetic behavior of Co nanowires arrays in AAO templates (200 nm pore diameters). From the hysteresis loops (BH), Garcia et al. concluded that even though the Co nanowires arrays showed magnetic anisotropy with the easy axis parallel to the wires, the coercivity was a minimum in that
direction. In their study, Garcia et al. demonstrated that the decrease in coercivity was due to the magnetic interactions between the nanowires.

Kautek et al. (Kautek, 1995) studied the fabrication of Au nanowires in track-etched PC membranes of different pore sizes ranging for 100 to 600 nm. Pulsed laser deposition technique was used to apply Au film on one side of the PC membrane. Using a double pulse potentiostatic scheme, Kautek et al. grew Au nanowires using an electrochemical jet cell having controlled fluid dynamics and an online coulometer. Kautek et al. concluded that the 400 nm diameters Au nanowires were obtained only when the membrane bottom pores were completely sealed by vapor deposition, otherwise “fragile and hollow basses” were observed.

Thurn-Albrecht et al. (Thurn-Albrecht, 2000) showed a different method of making nanowires by electrodeposition into self-assembled copolymer templates. Starting with self-assembled diameter diblock copolymers of polystyrene and polymethylmethacrylate (PMMA), after annealing, applied electric field, and deep ultraviolet exposure, the resulting polymer film contained 14 nm diameter pores inside which Co and Cu nanowires were successfully electrodeposited. Magnetic properties of the obtained Co nanowires showed that array regularity had a tremendous effect on the coercivity. According to their study, highly irregular arrays showed accidental spin switching, so-called recording media noise. Thurn-Albrecht et al. concluded that the self-assembled copolymer method could overcome the nanowires’ disorder observed in PC membranes that led to decreased coercivity. Furthermore, the authors showed that using the PMMA template method, both the pores aspect ratio and the distance between the wires could be adjusted.

Valizadeh et al. (Valizadeh, 2001) investigated the concentration distribution during the electrodeposition of Co nanowires into PC membranes (250 nm pore diameter and 20 m length). During the wires growth, Valizadeh et al. could identify two separate electrodeposition
regions: at the bottom of the membrane (short time) and almost filled pores. Valizadeh et al. determined that, for short times, the limiting current was given by Cottrell’s expression (\(i_{\text{lim}} \sim t^{-1/2}\)), and the Co diffusion coefficient was calculated to be \(D_{\text{Co}} = 2.5 \times 10^{-5} \text{cm}^2/\text{s}\). At longer times, a steady state diffusion controlled current, obtained by the overlapping of the individual nanowires diffusion zones, was given by a different expression (\(i_{\text{lim}} \sim 1/(r+L)\)). Investigation of the magnetic properties of Co nanowires showed improved coercivity values compared to bulk Co, with a preferred magnetic field parallel to the wires axis. Valizadeh et al. concluded that for large diameter wires, multi-magnetic domains were present when there was no exterior magnetic field applied.

AlMawlawi et al. (AlMawlawi, 1991) fabricated Fe nanowires by ac electrolysis deposition into self-prepared AAO templates of different diameters, ranging from 20 to 180 nm. For the magnetic characterization of the Fe nanowires, AlMawlawi et al. concluded that nanowire coercivity strongly depended on the wire aspect ratio and less on the membrane pore density. Furthermore, AlMawlawi et al. pointed out that Fe nanowire coercivity showed no anisotropy, being only a function of the aspect ratio.

Vila et al. (Vila, 2002) were the first to investigate the magnetoresistance (MR) and magnetic transport behavior of isolated Co nanowires. After being electrodeposited in PC (60 nm diameter pore) membrane, the Co wires were removed from the membrane and Electron Beam Lithography (EBL) was used to make contacts along individual wires. EBL gave the capability to obtain information on different segments along the same wire. From the AMR (Anisotropic Magneto Resistance) measurements of a single Co nanowire, Vila et al. concluded that the remanent magnetization did not depend on the direction of the applied field. Moreover the remanent magnetization was much different along the same wire, which could explain the
vanishing magnetoresistance problems and resistance jumps observed when the measurements cover an array of microns long wires.

Garcia et al. (Garcia, 2002) reviewed the MFM (magnetic force microscopy) studies done on nanowires, and emphasized that Co nanowires, 35 nm in diameter, revealed single magnetic domains. Larger diameter wires showed multiple magnetic domains, which caused magnetic disorder. In their study they emphasized the use of nanowires as MFM probes.

In a recent review, Sellmyer et al (Sellmyer, 2001) analyzed transition metal arrays of nanowires electrodeposited in self-assembled aluminum oxide membranes. They concluded that porous aluminum oxide templates, obtained by electrochemical anodization of aluminium in acidic electrolytes, were excellent mediums for nanowires electrodeposition due to high pore density, uniform pore distribution and high aspect ratios. Sellmyer et al. showed that large aspect ratio Co, Ni and Fe nanowires showed magnetization anisotropy, having an easy magnetization axis along the wires axis and 0.9 remanence ratios. The maximum coercivity was shown by Fe nanowires (3000 Oe), followed by Co nanowires (2600 Oe) and lastly by Ni nanowires (950 Oe). In their review, Sellmyer et al. highlighted the crucial effect of wire imperfections which led to the curling behavior, controlling the nanowires coercivity and magnetic viscosity. Using a magnetic model simulation, Sellmyer et al. also showed wire interactions could be approximated by a demagnetizing field.

2.3 Alloy Nanowires

Schwarzacher et al. (Schwarzacher, 1999) prepared heterogeneous CoCu nanowires in AAO templates (20 nm diameter) by galvanostatic electrodeposition. The researchers showed that, for heterogeneous nanowires, the coercivity decreased with annealing temperature and pressure, due to phase separation that generated larger Co-rich particle size.
Fedosyuk et al. (Fedosyuk, 1999) also researched heterogeneous CoCu alloy nanowires grown in AAO membranes of 20 nm pore diameter. The alloy nanowires showed room temperature GMR of less than 1 %, which slightly increased after annealing. In their study, Fedosyuk et al. remarked that the GMR shape changed drastically when the field was applied perpendicular or parallel to the wire axis. The magnetic behavior dependence on the field direction demonstrated that the wires exhibit magnetic anisotropy. Furthermore, it was concluded that the nanowire geometry greatly influenced their magnetic properties. Fedosyuk et al. also commented on the AAO membrane temperature resistance compared to PC membranes, but they pointed out the difficulty of AAO nanowires examination due to the more complicated membrane dissolution.

Blythe et al. (Blythe, 2000) further investigated heterogeneous Co_{20}Cu_{80} alloy grown by galvanostatic electrodeposition in the shape of nanowires, using two different sizes AAO membranes: 200 nm and 20 nm pore diameters. Their publication mentioned that heterogeneous nanowires alloys showed GMR at room temperature, but they do not provide any values. Blythe et al. concluded that there was a non-uniform distribution of large and very fine magnetic clusters along the deposited alloy nanowire, which led to high anisotropy in the demagnetizing field. Also, Blythe et al. mentioned that the high-ratio magnetic nanowires showed a broader range of magnetic clusters compared to a thin film of similar composition.

Zhu et al. (Zhu, 2001) studied the effect of applied magnetic field during CoNi alloy nanowire electrodeposition in AAO templates (200 nm pore diameter). Their examination showed that the perpendicular applied magnetic field during electrodeposition not only reduced the (BH) saturation fields, but also enhanced squareness. In a different study, Zhu et al. looked at magnetic properties of FeNi nanowires of very high aspect ratios (>1000). The FeNi nanowires were electroplated in self-prepared AAO of highly ordered pores (43 nm pore diameters and 60
nm distance between pores). Enhanced coercivity of 769 Oe and 70 % remanent magnetization was observed when the magnetic field was applied parallel to the wires.

Wang et al. (J. B. Wang, 2001) analyzed the structure and magnetic anisotropy of compositionally modulated FeNi alloy nanowires electrodeposited in AAO. Using XRD and Mossbauer spectroscopy, the obtained wires (16 nm diameter and 4 m length) showed a polycrystalline structure along the (110) direction. The Fe component proved to have magnetic moments parallel to the wires in contrast to bulk Fe that showed (100) as the easy magnetization axis. The authors stated that the change in the preferred magnetization axis was due to the large shape anisotropy. Moreover, Wang et al. confirmed that the Ni component showed a disordered placement along the wires.

Pena et al. (Pena, 2001) researched the electrodeposition of multi-material (conductor-semiconductor) nanowires, such as Au-CdSe-Ni-Au, Au-Ni-CdSe-Ni-Au, Au-CdTe-Au, and Au-CdTe-Ag-Au, using 200 nm pore diameter AAO commercial templates. The conductive and semiconductive elements were electrodeposited from separate baths; Au, Ni, Ag under galvanostatic control, while the semiconductors (Cd, Te, Se) were electrodeposited by cyclic voltammetry at a high scanning rate (750 mV/s) with a deposition rate of 2 A/scan. Pena et al. showed the ability to incorporate semiconductor portions along metallic wires, and investigated the respective changes in the wires electrical properties.

Wang et al. (Y. W. Wang, 2002) used in-house prepared AAO membranes (60 nm pore diameter) to electrodeposit CoAg alloy nanowires and study the annealing effect on magnetic properties. The coercivity was larger for the parallel magnetic measurements, and it also increased with increasing annealing temperature, due the isolation of single Co magnetic domains. A maximum parallel field coercivity of 183 Oe was reached at a critical maximum annealing temperature of 400 °C, after which the coercivity decreased sharply with temperature.
due to Co particle contraction. The perpendicular magnetic measurements showed much smaller coercivity values, and it did not improve with annealing temperature. Wang et al. concluded that CoAg alloy nanowires showed anisotropic coercivity that could be optimized with an appropriate annealing temperature.

Qin et al. (Qin, 2002) investigated the annealing effect on coercivity and squareness of CoNi alloy nanowires electrodeposited in self-made high pore density AAO (20 nm pore diameter). Qin et al. observed that the crystalline difference of CoNi alloy grains from the bulk Co contributed a great deal to the magnetic behavior. Since the Co only nanowires showed high magneto crystalline anisotropy, which competes with the wire shape anisotropy, reduced squareness. In the case of CoNi alloy nanowires, the shape anisotropy reflected more on the squareness. Furthermore, the squareness was increased for high concentrations of Ni (>50 %) in the alloy. The parallel field coercivity saw a maximum of 950 Oe for low Ni content (>10 %), and decreased with higher Ni content. Qin et al. concluded that the annealing treatment lowered the coercivity values but increased squareness.

Wang et al. (Wang, 2002) revised the structural profile and magnetic behavior of Ni_{50}Cu_{50} alloy nanowires electrodeposited in high aspect ratio AAO (50 nm diameter/ 50 m length). Parallel magnetic anisotropy was observed. The author pointed out that the Ni atoms in the NiCu alloy wires did not show a proportional, structured placement pattern because the wire electrodeposition was not at steady state.

Khan and Petrikowski (Khan, 2002) investigated the Co and CoFe alloy nanowires electrodeposited in AAO, and compared the wires magnetic properties to the thin film alloy of similar composition. High aspect ratio CoFe nanowires (18 nm pore diameter and 3 m length) were obtained, and were compared to the 1-2 m thin films electrodeposited on Cu substrate from the same electrolyte. The Co_{90}Fe_{10} alloy nanowires held the highest parallel coercivity
(2275 Oe) followed by the Co only nanowires that showed a smaller coercivity (1188 Oe). Conversely, the Co only thin film had a larger perpendicular coercivity (288 Oe) than the Co90Fe10 thin film (187 Oe), while all the nanowires cases had significantly higher coercivity compared to the thin films. In a latter study, Khan and Petrikowski showed that parallel magnetic anisotropy, coercivity and squareness decreased drastically with increasing pore diameters (HcCo90Fe10 = 2275 Oe (18 nm pore diameter) and HcCo90Fe10 = 723 Oe (78 nm pore diameter)).

In a different study, Fodor et al. (Fodor, 2002) researched compositionally modulated CoFe alloy nanowires in AAO. They observed that at low Fe concentration in the alloy (>10%), cobalt crystalline arrangement changed from HCP to FCC, while at higher concentrations of Fe (>15%) the cobalt crystalline arrangement switched to a BCC structure. The largest observed coercivity (2150 Oe) was measured for a Co45Fe55 alloy, which had no crystal anisotropy (BCC arrangement). Fodor et al. mentioned the significant magnetostatic interactions between wires, which could be explained by dipolar stray fields opposing each other and reducing the field necessary to reverse magnetization.

Ross et al. (Ross, 2002) wrote a review for small aspect ratio alloy nanowires obtained by a combination of interface lithography and electrodeposition. The electrodeposition takes place inside a porous polymer layer (57-180 nm pore diameters) set on a silicon wafer coated with gold. After electrodeposition, cylindrical geometries (300 nm tall) were obtained after the template removal. Magnetic Force Microscopy (MFM) proved that small diameter structures showed high remanence, vital for information readback processes. In contrast, the large diameter wires showed low remanence. Ross et al. pointed out that magnetostatic interactions between wires controlled the magnetic behavior of highly packed arrays, which generated instantaneous demagnetization. Ross et al. concluded that larger coercivity values, which were needed to avoid
instantaneous demagnetization, were obtained for single domain structures observed only in small diameters wires.

Sellmyer et al. (Sellmyer, 2001) summarized in review the influence of electrolyte additives on the coercivity and squareness ratios of alloy nanowires. They showed that coercivity increased linearly with increasing Fe content in Ni-Fe alloy nanowires. In the same review, Sellmyer et al. mentioned that the addition of Cu and phosphor to the Fe nanowires decreased their coercivity under 1000 Oe.

Very recently, Bai and Hu (Bai, 2003) reported making FeCo and FeCoNi alloy nanowires by cyclic voltammetry and pulse reverse electrodeposition. Surprisingly, Bai and Hu did not use any porous membrane for electrodeposition. Bai and Hu explained that the anodic cyclic voltammetry guided the formation of nanowires on a flat Cu plate. Furthermore, adding Ni to the electrolyte showed an increase in wires diameter.
CHAPTER III EXPERIMENTAL PROCEDURES

Electrodeposition occurs when a current passes through an ionic solution. At the cathode reduction takes place and pure metal forms according to:

\[ M^{n+} + n \, e^- \rightarrow M(s) \]

Figure 3.1 illustrates the three-electrode cell set-up used in this study. A platinum mesh was used as the anode (or counter electrode). A saturated calomel electrode (SCE) functioned as the potential reference. The membranes were sputtered on one side with gold for electrical contact.
Two types of porous membranes, polycarbonate (PC) Millipore Isopore\textsuperscript{TM} and aluminum oxide (AAO) Whatman Anodisc were used to make the nanowires. A wide range of pore sizes (20-800 nm) was tested. The nanowires were deposited at the cathode in a porous membrane. Figure 3.2 shows a porous membrane schematic that illustrates the random nature of the pores. The membrane was fixed inside a stationary peek holder exposing a square area of $2.25 \text{ cm}^2$ of the membrane.

![Figure 3.2 Porous membrane schematic: www.inginerie.ro](image)

Different electrolytes and plating schemes were investigated for the nanowire deposition. DC plating and pulse plating was carried out with a PC controlled Solatron (model SI 1287). Electrolyte polarization studies, cyclic voltammetry at different sweep rates and impedance measurements were performed using the Solatron (model SI 1287).

In order to release the nanowires for further investigation, the polycarbonate membranes were soaked in dichloromethane, and the aluminum oxide ones were exposed to 1M NaOH solution for 1h. The membrane etching process is shown below in Figure 3.3.
After dissolving the membrane, the arrays of nanowires were imaged using Scanning Electron Microscope (SEM-JEOL JSM-840 operated at 20 kV) and Transmission Electron Microscope (TEM JEM-100CX operated at 80 kV). The SEM technique scans the specimen with a focused beam of electrons and produce secondary electrons that are detected and converted into an image. TEM examination involves passing the electron beam through the sample, and can obtain a higher magnification than the SEM technique. The electrons very short wavelength makes it possible to obtain high resolutions. The SEM was used to inspect arrays of nanowire, while the TEM was utilized to examine nanowires layers and nanotubes formation.

Composition analysis of the nanowire arrays was obtained using Energy Dispersive Spectroscopy (SEM-EDS) and X-Ray Fluorescence Analyzer (XRF KEVEX Omicron). SEM-EDS provides a qualitative composition analysis, which uses a stream of high-energy electrons to knock off specimen’s inner shell electrons. On contact, electrons from a higher energy level lose energy filling in the vacancies left. The energy conservation principle dictates photon creation. The released photon energy will be equal to the difference of the two exchanged energy levels. Since these energy levels are unique for an atom type, the released photon will be characteristic of the type of atom from which it was emitted. Therefore, from the released photon energy, the sample composition is determined. SEM-EDS analyses a spot size of about 1 μm.
XRF was employed to obtain the quantitative average composition analysis of the nanowire array. The XRF analysis is based on a primary x-ray tube that emits characteristic x-rays of known energy. An electron can be ejected from its atomic orbital by the absorption of a light wave (photon) of sufficient energy. Any elements in the sample having excitation energy below that of the primary beam energy will be fluoresced. The particular wavelength of fluorescent light emitted is related to the number of photons per unit time, (peak intensity or count rate) and to the amount of the specific element in the sample. Therefore, by determining the energy of the X-ray peaks and by calculating the count rate of the various elemental, it is possible to quantitatively measure the concentration of these elements in the sample.

The magnetic properties, such as GMR and coercivity, were investigated with PPMS (Quantum Design Physical Property Measurement System 6000) using an electric current ranging between 0.1-1 mA and a magnetic field in between –2 T to 2 T. All measurements were performed at room temperature. In the GMR set-up, the magnetic field was set perpendicular to the electric current passing through the nanowires, the magnetic field being parallel to the layers.
CHAPTER IV NANOWIRE RESULTS AND DISCUSSION

4.1 Electrolyte Characterization

At equilibrium, each reaction is characterized by a reversible potential (E_{rev}). The more negative the reversible potential, the more difficult an element is to deposit. The standard reduction potentials of the four elements present in the electrolyte are given in Table 4-1-1.

Table 4-1-1 Standard reduction potentials

<table>
<thead>
<tr>
<th>Electrochemical Reactions</th>
<th>Standard Equilibrium Potentials V vs. Normal Hydrogen Electrode (NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu^{2+} + 2e----&gt; Cu</td>
<td>0.3419</td>
</tr>
<tr>
<td>Ni^{2+} + 2e----&gt; Ni</td>
<td>-0.257</td>
</tr>
<tr>
<td>Co^{2+} + 2e----&gt; Co</td>
<td>-0.28</td>
</tr>
<tr>
<td>Fe^{2+} + 2e----&gt; Fe</td>
<td>-0.447</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Side Reactions</th>
<th>Standard Equilibrium Potentials V vs. Normal Hydrogen Electrode (NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ +4H⁺ + 4e----&gt; 2 H₂O</td>
<td>1.229</td>
</tr>
<tr>
<td>2H⁺ + 2e----&gt; H₂</td>
<td>0</td>
</tr>
<tr>
<td>2H₂O +2e----&gt; H₂ +2OH⁻</td>
<td>-0.828</td>
</tr>
</tbody>
</table>

Inspection of Table 4-1-1 shows that Cu would reduce first, long before the Ni, Co, Fe. Since Cu can be easily reduced, the concentration of Cu in the electrolyte was kept low, in order to have Cu deposition under mass transport control, while all the other elements (CoNiFe) would be deposited under kinetic control. The schematic below shows the deposition strategy:

![Figure 4.1.1 Elements electrodeposition regimes](image-url)
The iron group alloy deposition is also called anomalous codeposition, since the least noble element (Fe) tends to deposit before the Ni and Co, even thought these elements have a more positive reduction potentials than Fe. To limit the preferential Fe deposition, the Co and Ni concentrations in the electrolyte were set much larger than Fe’s concentration. The initial electrolyte (concentrated bath) is shown in Table 4-1-2:

Table 4-1-2 Concentrated CoNiFeCu electrolyte

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSO₄</td>
<td>500</td>
</tr>
<tr>
<td>NiSO₄</td>
<td>500</td>
</tr>
<tr>
<td>FeSO₄</td>
<td>100</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>10</td>
</tr>
<tr>
<td>Na-K Tartrate</td>
<td>100</td>
</tr>
<tr>
<td>Ascorbic Acid</td>
<td>20</td>
</tr>
</tbody>
</table>

In order to characterize the deposition, polarization curves of the electrolyte were performed using an empty PC membrane as the cathode. The influence of mixing, in the form of N₂ bubbling, was studied. Figure 4.1.1 shows current-potential curves for different mixing/bubbling cases. A sweep rate of 5 mV/s was used to generate all polarization curves. An ohmic drop of 15 ohms was accounted for when the current vs. potential curves were generated, therefore the potential shown was the working potential.

From the polarization curves, it was deduced that the optimal case was the no bubble scenario that would keep the Cu limiting current to a minimum. Figure 4.1.2 shows the Cu limiting current increasing when agitation was introduced in the system. In the no-mixing (no bubble) scenario the average Cu limiting current (–0.9 mA) was lower than both the average Cu limiting current in the (medium-bubble -1.1 mA) and in the (high-bubble –1.7 mA) cases.
Figure 4.1.2 Concentrated CoNiFeCu electrolyte polarization curves (Variable degree of agitation)
Unfortunately, the concentrated bath turned out to be unstable, showing precipitation over time. For this reason, we decided to investigate the same bath components but in a diluted version. The diluted electrolyte composition is shown in Table 4-1-3.

Table 4-1-3 Diluted CoNiFeCu electrolyte

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>main components</td>
<td></td>
</tr>
<tr>
<td>CoSO₄</td>
<td>50</td>
</tr>
<tr>
<td>NiSO₄</td>
<td>57</td>
</tr>
<tr>
<td>FeSO₄</td>
<td>8</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>1</td>
</tr>
<tr>
<td>additives</td>
<td></td>
</tr>
<tr>
<td>Na-K Tartrate</td>
<td>27</td>
</tr>
<tr>
<td>Sulfamic Acid</td>
<td>10</td>
</tr>
<tr>
<td>Na-Saccharin</td>
<td>4</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>0.6</td>
</tr>
</tbody>
</table>

A polarization curve without agitation was also run for the diluted electrolyte, using the same potential sweep rate of 5 mV/s and a PC membrane as the cathode.
Impedance measurements were performed and the ohmic drop was accounted for. From Figure 4.1.3, the Cu limiting current was deduced to be around 1.1 mA, while the CoNiFe alloy limiting current was observed to be 25 mA.

From the above polarization curve, the Cu deposition potential was distinguished to be between -0.25 V and –0.6 V, while the alloy deposition potential showed a more negative range of potentials (-1.5 V to –4 V).

To determine the optimal conditions at which either mostly Cu or CoNiFe alloy would deposit, several constant potential depositions were performed on Au flat plate. The composition of Cu is shown in Figure 4.1.4. The data is listed in the Appendix.

From these constant potential trials on the Au flat plate, the most pure Cu deposit was obtained at a constant potential of –0.325V, while the minimum Cu content in the CoNiFeCu alloy was obtained for a constant potential of –2.1V. Figure 4.1.4 shows graphically the Cu content as a function of applied potential.

Figure 4.1.4  Diluted CoNiFeCu bath polarization curve without agitation
In the less negative potential region, between –0.3 V and –0.5 V, the deposit was mostly Cu (98 wt%). Alternatively, in the more negative potential region, between –1.6 V and –2.4 V, the Cu content was minimal (1%), therefore the deposit was mostly CoNiFe.

Knowing the deposit composition, thickness and duration, Faraday's Law was applied to calculate the partial currents of bath components. According to Faraday’s Law, the electrodeposition rate is related to the current passed:

$$\frac{\varepsilon \cdot I}{n \cdot \text{Faraday}} = \frac{m}{\text{MW} \cdot t}$$

\( I = \) observed current
\( n = \) number of electrons
\( F = \) Faraday's constant
\( \varepsilon = \) efficiency
\( m = \) mass plated
\( \text{MW} = \) molecular weight
\( t = \) plating time

Tabulated calculations, for finding the Co, Ni, Fe and Cu individual currents as a function of potential, can be found in the Appendix.
The partial current densities are shown in Figure 4.1.5. Due to the low Cu concentration in the electrolyte, the Cu limiting current was clearly observed at –0.5 V vs. SCE.

The Co limiting current was higher than the Ni limiting current, even though the Ni had the highest concentration in the electrolyte. Although Fe was kept in much smaller quantities in the bath, its limiting current was comparable to the Ni limiting current, confirming the anomalous codeposition behavior of CoNiFe.

Figure 4.1.6  Partial currents of individual species present in the electrolyte
4.2 Nanowire Electrodeposition

From the flat plate electrodeposition, the Cu ideal potential was found to be (–0.325 V) while the CoNiFe alloy potential chosen to be (–1.9 V). In order to test the ability of making nanowires, the flat plate conditions for alloy and Cu were used in a series of experiments with polycarbonate membranes of different sizes. The polycarbonate membrane fabrication involves a nuclear track etch process, which arises from a bombardment of the polycarbonate film with high-energy particles which produce the paths which later are etched in different chemical baths. This etching process determines the size of the pores. Typical pore sizes range from 20 nm to 14 µm. Figure 4.2.1 shows a SEM picture of a commercial PC membrane, having a reported pore size of 800 nm.

![Figure 4.2.1 Nucleopore PC membrane](image)

Although the pores seem to have similar diameters, the pore placement is random. In addition, a common problem with PC membranes is the observed pores fusion and branch-like structures at one end of the membrane. However, due to the elasticity of polycarbonate, the internal stress in the plated metal nanowires is reduced.
4.2.1 Nanowires in PC Membrane

Starting with larger pores templates, 200 nm pore diameters Nucleopore PC membrane, alloy nanowires were deposited using constant potential of –1.9 V. After dissolving the template in dichloromethane, the wires were imaged using SEM, Figure 4.2.2. A disparity was observed between the manufacturer specifications and the actual pore sizes. Under SEM examination, the commercial available membranes also showed branching at one end.

Thinner wires were fabricated using smaller pore membranes, such as 100 nm pore diameter Isopore PC membranes. Using the same alloy deposition conditions, nanowires were deposited using constant a potential of –1.9 V vs. SCE. A low magnification SEM illustrates a
forest of CoNiFeCu nanowires, Figure 4.2.3 (a). Transmission Electron Microscope (TEM) was employed to examine a single nanowire, Figure 4.2.3 (b). In order to make higher aspect ratios (length to diameter) nanowires, smaller pore membranes were employed. Keeping the same constant potential (-1.9 V) alloy deposition conditions, Whatman Nucleopore PC membranes having 50 nm pores were used as templates.

Figure 4.2.4 (a) displays a SEM micrograph of the CoNiFeCu nanowires held together by the Au sputtered side of the membrane. Figure 4.2.4 (b) shows a higher magnification SEM picture of the CoNiFeCu nanowires in a partially dissolved membrane. The same alloy nanowires were also imaged by TEM. Figure 4.2.4 (c) shows that the CoNiFeCu nanowires were 150 nm in diameter and 5-micrometer in length.
The EDS spectrum, shown below in Figure 4.2.5, gives a qualitative composition analysis of the alloy nanowires, indicating the presence of Co, Ni, Fe and Cu.

Figure 4.2.4 CoNiFeCu nanowires in Whatman Nucleopore PC membrane
a) Low magnification SEM b) higher magnification SEM c) TEM

Figure 4.2.5 Alloy nanowires EDS
An overall quantitative composition analysis of the alloy nanowires was obtained using the KEVEX Omicron energy dispersive X-ray fluorescence analyzer (XRF). The CoNiFeCu nanowire sample electrodeposited at (-1.9 V vs. SCE) showed 62-wt% Co, 28-wt% Ni, 8.5-wt% Fe and 1.5-wt% Cu.

Using the 50 nm Whatman PC membranes, a series of alloy nanowire deposition experiments were performed using different constant potentials. Figure 4.2.6 shows the current behavior as a function of potential during nanowires deposition.

![Figure 4.2.6 Nanowires transient currents at different potentials](image)

The current versus time plots show that the nanowire deposition is not a steady state process. When the pores were empty the current dropped suddenly and reached an almost steady state when the wires were growing. The current gradually increased with the filling of the pores and reached a steady state when the wires reached the top of the membrane. As the deposition continues, the deposition area is constant and the resulting current is constant. Given the
membrane thickness, it was possible to calculate the time it would take to fill up the pores with nanowires. In the case of CoNiFeCu alloy nanowires, Figure 4.2.6 shows that the 6-micron deep pores would be filled in 700 sec, using a constant potential of –1.9 V vs. SCE.

To estimate the time it would take to make Cu only nanowires, a constant potential of (–0.5 V vs. SCE) was applied for 8 hours. Figure 4.2.7 shows the current behavior during Cu deposition in the PC template.

![Figure 4.2.7 Cu nanowires electrodeposition in 50 nm pores PC membrane](image)

During Cu deposition at -0.5 V constant potential, the current density was lower than for the alloy nanowire case, therefore the time to fill up the pores was approximately 5000 seconds, much longer than in the alloy case. The long transient region at the start of the deposition is due to the change of the concentration gradient due to the diffusion of Cu.
4.2.2 CoNiFeCu/Cu Multilayered Nanowires

A schematic of an array of multilayered nanowires is shown in Figure 4.2.8.

Multilayers were deposited into the pores with the conditions determined from the previous section. The Cu and alloy mass electrodeposited was estimated from the unlayered deposit. Faraday’s law was used to calculate the theoretical time to fully grow the wires. The current efficiency was determined by comparing the calculated time to the observed experimental time to grow the nanowires. In the PC membrane, the Cu nanowires current efficiency was 43 %, higher than the CoNiFe alloy nanowires current efficiency of 26 %.

Similarly, the electrodeposition time to deposit one nanometric layer of known thickness was calculated by taking the ratio between the layer thickness and the nanowires length, and multiplying it by the time it took to fully grow Cu or alloy nanowires. The number of bilayers (Cu/CoNiFe) that would fill up the membrane with multilayered nanowires was then estimated. Detailed MathCAD calculations are included in the Appendix. Switching between the CoNiFe and the Cu deposition potentials, alternating alloy and Cu layers is achieved from the same electrolyte, as illustrating in Figure 4.2.9.
Using a potentiostatic square wave, the CoNiFeCu alloy potential was held at –1.9 V while the Cu potential was maintained at –0.5 V. Different layer times were tested and resulting layer thickness compared. After deposition, the PC membranes were dissolved for TEM examination.

Figure 4.2.10 illustrates different CoNiFeCu/Cu layer sizes deposited in 50nm pore diameter PC membranes. In Figure 4.2.10 (a) the CoNiFe layer is quite large (550 nm) while the Cu layer is 40nm. In Figure 4.2.10 (b) the alloy CoNiFe layer is about 200 nm thick and the Cu layer is much thinner (20 nm). Figure 4.2.10 (c) shows much thinner (20 nm) CoNiFe alloy layers alternating with 20 nm Cu layers. The TEM micrographs show the wire diameter to be around 100 nm, rather than 50 nm diameters specified by the manufacturer. From the lower magnification TEM pictures, the wire length was observed to be around 5 microns, which indicates that the wires were completely grown.
CoNiFeCu alloy layer potential: -1.9 V for 100 sec yielded 550 nm observed layer thickness
Cu layer potential: -0.5 V for 500 sec yielded 40 nm observed layer thickness

CoNiFeCu alloy layer potential: -1.9 V for 20 sec yielded 200 nm observed layer thickness
Cu layer potential: -0.5 V for 200 sec yielded 20 nm observed layer thickness

CoNiFeCu alloy layer potential: -1.9 V for 10 sec yielded 20 nm observed layer thickness
Cu layer potential: -0.5 V for 100 sec yielded 15 nm observed layer thickness

Figure 4.2.10 Different NiCoFeCu/Cu layer ratios in PC membrane (50 nm pore diameter)
The micrographs also show that layer thickness changes along the wires, being smaller at the bottom and gradually increasing towards the top of the membrane. This change in layer thickness along the wires is due to the change in diffusion layer thickness. When bulk multilayered nanowires were examined, the EDS spectrum verified the deposition of Co, Ni, Fe and Cu, Figure 4.2.11.

![Figure 4.2.11 CoNiFe/Cu nanowires EDS](image)

4.2.3 Nanowires in Aluminum Oxide (AAO) Membranes

Anopore Aluminum Oxide (AAO) membranes were also employed as templates for nanowires electrodeposition. AAO filter preparation involves an anodic potential applied to aluminum foil in an acidic environment. Under electrochemical control, the membrane pores could be controlled. Commercially available Anopore AAO membranes having 20 nm pore diameters were used for nanowires deposition.

Employing the same electrolyte used in PC nanowires, previously used deposition conditions for Cu were tested for nanowires fabrication in the AAO templates. Figures 4.2.11 shows a SEM micrograph of nanowire arrays plated at a constant potential of (–0.325 V) versus SCE. At this Cu potential, the nanowires were found to be fully-grown, 60 micrometers in length. The wire diameter was observed to be 180 nm, much larger than the manufacturer’s specifications of 20 nm. The EDS spectrum in Figure 4.2.12 confirmed the wires were pure Cu.
Figure 4.2.11 Cu nanowires in Anopore aluminum oxide membranes

Figure 4.2.12 EDS spectrum for Cu nanowires in AAO (-0.325V)
From the current response during potentiostatic deposition of Cu nanowires at a constant potential of (–0.325V) vs. SCE, it is clear that nanowires reached the top of the membrane after 70000 sec, when the current achieved steady state (-1.2 mA), Figure 4.2.13.

FeCoNiCu alloy nanowires were also deposited using potentiostatic control at a more negative potential (–2V) versus SCE. Figure 4.2.14 (b) shows a SEM micrograph of the CoNiFeCu nanowires after dissolving the AAO membrane. The EDS spectrum, Figure 4.2.14 (a), shows that traces of Cu were present in the deposit.

Figure 4.2.13 Current response for potentiostatic deposition of Cu

Figure 4.2.14 Alloy nanowires in AAO a) EDS spectrum b) SEM picture
Figure 4.2.15 shows the current response at CoNi electrodeposition potentials (-1.9 V), when alloy nanowires are plated inside AAO membrane. The current arrives at steady state (-0.015 A) when the nanowires reach the top of the membrane, after 7000 sec.

![Figure 4.2.15 Current response for potentiostatic deposition of CoNi nanowires in AAO](current_response.png)

**4.2.4 Multilayered (CoNi(Fe)/Cu) Nanowires in (AAO) Membranes**

Similar to the procedure used for the PC membrane nanowires, the theoretical time to deposit Cu or alloy nanowires was calculated using Faraday’s Law. Since the pores dimensions and observed currents have changed in the AAO case, the nanowires mass and deposition time were also different. The Cu current efficiency in AAO membranes was 62 %, higher than the CoNiFe alloy current efficiency of 18 %. The detailed MathCAD layer calculations can be found in the Appendix.

Using the above layer calculations, a potentiostatic pulse scheme was employed for CoNiFeCu/Cu multilayered nanowires. As shown in the Figure 4.2.16 schematic, the Cu layer
deposits at a controlled potential of -0.325 V vs. SCE, while the Co rich (CoNiFe) layer forms at a more negative potential -1.9 V vs. SCE.

Note that the alloy layer would also contain traces of Cu. As shown in Figure 4.2.16 a larger transient current region can be observed during Cu layer deposition. Switching from the CoNiFe potential (-1.9 V) to the more noble Cu potential (-0.325 V), the current transitions though an anodic (positive) region until it settles down to the Cu deposition current (-0.001A).

Figure 4.2.16 Potential pulse and current response

Figure 4.2.17 Potentiostatic Pulsing Charge Control Scheme
The anodic current will dissolve some of the Co rich layer previously deposited. To ensure that the anodic current would not dissolve the entire CoNiFe layer, different electrodeposition pulse techniques were investigated.

Charge deposition, which equals to the applied current times the deposition time, was monitored so that the portion of anodic Cu current would be negligible compared to the alloy deposition current. Figure 4.2.17 shows the charge control electrodeposition technique for multilayers formation. To avoid the anodic current region, a combination of galvanostatic/potentiostatic pulses was employed. The alloy layer was potentiostatically controlled at (-1.9 V) and the Cu layer galvanostatically controlled at (-0.001 A). Figure 4.2.18 shows a sketch of this combined electrodeposition method for fabricating multilayers.

Due to the Fe anomalous codeposition effects on the nanowires magnetic properties, the electrolyte was simplified by removing the Fe, while keeping all the other conditions unchanged. Using potentiostatic pulse plating, the CoNiCu alloy layer was deposited at (–1.9 V vs. SCE) for a period of 1 second, while the Cu layer was deposited at (–0.325 V vs. SCE) for 15 seconds.

Figure 4.2.19 presents the current response to the double potentiostatic pulse deposition. The anodic current was still observed but the dissolution charge from the anodic current was small compared to the deposition charge in the CoNi high negative potential pulses.
Figure 4.2.19 CoNiCu/Cu potentiostatic pulsing current response

Figure 4.2.20 CoNiCu/Cu nanowires in AAO
After the 2400 bi-cycles of alloy/Cu layers, the deposition was stopped and the membrane was dissolved in order to examine the nanowires. TEM was used to image the layered wires. Distinct CoNi alloy layers (dark) alternating with pure Cu layers (white) were observed. Figure 4.2.20 shows the TEM micrograph of the CoNiCu/Cu nanowires. The alloy layer was around 10 nm thick, while the Cu layer was about 8 nm thick. The layers seemed to grow in a concave shape.

4.3 Magnetic Measurements

Magnetic moments in a material arise from electron orbital motion, the change in orbital motion caused by an external magnetic field, and the electrons spin. Cu is a paramagnetic material, meaning there is a small and positive susceptibility to magnetic fields. Paramagnetic materials are slightly affected by a magnetic field and do not keep the magnetic character when the field is removed. Co, Ni and Fe are ferromagnetic materials and show a large positive susceptibility to an external magnetic field. At the atomic level, the unpaired electron spins align forming magnetic domains.

4.3.1 Coercivity Measurements

When a ferromagnetic material is magnetized in one direction, it will not relax back to zero magnetization when the imposed magnetizing field is removed. Coercivity is the amount of reverse driving force (magnetic field) required to demagnetize the material, as shown in Figure 4.3.1. The amount of magnetization the ferromagnetic material retains at no external magnetic field is called its remanence ($m_r$), and it is used in magnetic memory devices. Arrays of alloy nanowires have potential applications in perpendicular ultra-high density data storage due to their coercivity. CoNiFe and CoNiFeCu alloy nanowires were electrodeposited in PC membranes of 50 nm pore diameters. Controlling potential, different CoNiFeCu nanowires samples were electroplated at a high potential (-2 V) and at a lower potential (-1.5V). Each sample overall composition was determined by the XRF, Table 4-3-1.
Perpendicular and parallel coercivity measurements were performed. Hysteresis loops are shown in Figure 4.3.2. The CoNiFeCu sample plated at (–2V) showed 50G coercivity for both perpendicular and parallel measurements, Figure 4.3.2 (b). The CoNiFeCu sample plated at the lower potential (-1.5V) had slightly larger coercivity of 120G, Figure 4.3.2(a). Both samples showed no magnetic anisotropy. The larger coercivity, in the second sample plated at the lower potential (-1.5V), could be due to a higher Fe content (12 %) than the first sample (7 %). CoNiFe alloy nanowires, eliminating Cu, were plated at a high negative potential of (-2 V) and at a lower potential of (-1.5 V). The nanowires XRF composition is shown in Table 4-3-2.

<table>
<thead>
<tr>
<th>CoNiFeCu (-2V) XRF Analysis</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
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<tr>
<td></td>
<td>7%</td>
<td>58%</td>
<td>33%</td>
<td>2%</td>
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</table>

<table>
<thead>
<tr>
<th>CoNiFeCu (-1.5V) XRF Analysis</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>12%</td>
<td>70%</td>
<td>11%</td>
<td>6%</td>
</tr>
</tbody>
</table>

Table 4-3-1 CoNiFeCu alloy nanowires XRF

Perpendicular and parallel coercivity measurements were performed. Hysteresis loops are shown in Figure 4.3.2. The CoNiFeCu sample plated at (–2V) showed 50G coercivity for both perpendicular and parallel measurements, Figure 4.3.2 (b). The CoNiFeCu sample plated at the lower potential (-1.5V) had slightly larger coercivity of 120G, Figure 4.3.2(a). Both samples showed no magnetic anisotropy. The larger coercivity, in the second sample plated at the lower potential (-1.5V), could be due to a higher Fe content (12 %) than the first sample (7 %). CoNiFe alloy nanowires, eliminating Cu, were plated at a high negative potential of (-2 V) and at a lower potential of (-1.5 V). The nanowires XRF composition is shown in Table 4-3-2.

<table>
<thead>
<tr>
<th>CoNiFe (-2V) XRF Analysis</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7%</td>
<td>62%</td>
<td>31%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CoNiFe (-1.5V) XRF Analysis</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11%</td>
<td>72%</td>
<td>17%</td>
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</table>

Table 4-3-2 CoNiFe alloy nanowires XRF
The sample plated at the more negative potential showed the same coercivity value of 75 G for both in plane and perpendicular magnetic measurements. In Figure 4.3.3, the CoNiFe (-2 V) sample hysteresis loop is shown and no magnetic anisotropy can be observed.

Figure 4.3.2 CoNiFeCu alloy nanowires hysteresis a) –1.5 V  b) –2 V

The sample plated at the more negative potential showed the same coercivity value of 75 G for both in plane and perpendicular magnetic measurements. In Figure 4.3.3, the CoNiFe (-2 V) sample hysteresis loop is shown and no magnetic anisotropy can be observed.
The CoNiFe sample plated at the lower potential -1.5 V had larger coercivity, 110 G and showed magnetic anisotropy. The measurement perpendicular to the plane of the sample, which is the direction parallel to the wires axis, showed a larger coercivity value than the parallel measurement of 50 G. The samples showed magnetic anisotropy with an easy magnetization axis.

Figure 4.3.3 CoNiFe alloy nanowires hysteresis: (a) (–2V) (b) (–1.5V)
along the wires axis.

Figure 4.3.3(b) shows the CoNiFe sample plated at the lower potential -1.5 V. The electrodeposition potential was observed to influence the coercivity values and the magnetic anisotropy. The lower potential (-1.5 V) CoNiFeCu sample showed a larger coercivity value of 120 G, than the high potential (-2 V) CoNiFeCu sample that had a coercivity of 50 G.

The presence of Cu in the alloy modified coercivity values. When Cu was taken out of the magnetic alloy, the coercivity increased from 50 G in the CoNiFeCu sample, to 75 G in the CoNiFe sample, even though both samples were plated at the same high potential (-2 V).

4.3.2 GMR Measurements

Giant Magnetoresistance (GMR), a change in electrical resistance due to an applied magnetic field, is observed when ferromagnetic and nonmagnetic nanoscale layers alternate. The majority and minority electrons have different interface reflection coefficients, making the spin transport along the interfaces acting as a torque on the magnetization. This torque aligns the magnetization according to the reflection coefficients. Figure 4.3.4 shows a schematic of the theory behind the GMR principle.

Due to their intrinsic geometry, multilayered nanowires favor the study of perpendicular magneto-transport phenomena, CPP-GMR. The experimental set-up for magnetic measurements is shown below in Figure 4.3.5. Under no magnetic field, the nanowires antiferromagnetic-coupled multilayers show a certain resistance, which decreases when the nanowires sample is placed in a magnetic field.
Figure 4.3.4 GMR Schematic: The majority carriers become minority carriers in the adjacent magnetic layer. Increased electrical resistance is observed in antiferromagnetic arrangement.

\[ R_{H \neq 0} < R_{H = 0} \]

Figure 4.3.5 CPP GMR contacts
The electron spins of adjacent magnetic layers align under a certain magnetic field allowing the majority carriers to travel less scattered along the wires. Minimizing electron scattering across the layers, the magnetic field promotes electron travel, therefore decreasing electrical resistance.

4.3.2.1 CoNiFe/Cu in PC Membranes GMR

For the investigation of the GMR effect, multilayered nanowires of CoNiFeCu/Cu were electrodeposited in PC membranes with pores 200 nm in diameter (SEM observed). Using efficiency calculations, different Cu layer thicknesses were tested in order to optimize the GMR effect. Figure 4.3.6 shows several GMR measurements of nanowire samples electrodeposited using conventional potentiostatic pulsing. The Cu layer was plated at (-0.5 V vs. SCE), and alloy CoNiFe layer was deposited at (-2 V vs. SCE). The layer deposition time was based on a 43 % Cu current efficiency and a 26 % alloy current efficiency derived from bulk deposits, as described in Section 4.2.2.
Even though all plots show resistance time dependence, the thinnest (1nm) Cu layer sample exhibited the most resistance variance during the measuring time. It seems that the thicker Cu layer (3 nm) sample showed less change in resistance at zero magnetic field. Even when the sample’s resistance did not fluctuate in time as much as the other samples, the GMR behavior was still noisy and irregular. Various layer thicknesses for both Cu and alloy were tested, but the results were not satisfactory. Since the membrane pore sizes were quite large (200 nm), it could have favored the formation of multi magnetic domains inside a single magnetic layer. The presence of several magnetic domains in a layer could ruin the antiferromagnetic coupling for the GMR, which could explain the noisy response in resistance change with magnetic field. To eliminate the multi-domain possibility, PC membranes with smaller pore sizes (100 nm) were employed for the deposition of multilayered CoNiFe/Cu nanowires. Although the pores were much smaller, all the measured samples showed resistance variation in time even when no external magnetic field was applied. Even though the membrane pore sizes were smaller than in the previous case, they were still large enough to permit the magnetic multi-domain formation. Furthermore, the PC membranes showed large irregularities in pore sizes and pore shapes. Figure 4.3.7 shows the frequent pore overlapping. Figure 4.4.2 showed wire branching in PC membranes.

![Image](image.png)

Figure 4.3.7 Pore irregularities in PC membrane
The loss in GMR behavior could be attributed to nanowire interaction from overlapping pores. Non-distinct layers inside nanowires could also explain the irregular GMR. Another possibility, that could explain the loss of GMR, is the composition variation at the layers interface, which could be a consequence of the anodic dissolution of the Co layer during the transition from the higher negative potential to the lower Cu potential. To eliminate the anodic current transition, a combination of galvanostatic/potentiostatic electrodeposition technique was implemented, such that the Cu layer was deposited at constant current, and the alloy layer was deposited at constant potential. Unfortunately, this electrochemical strategy did not solve the resistance time dependence.

A different electrodeposition scheme, which introduces a relaxation period after each pulse, was adopted. Figure 4.3.8 shows the best GMR curve for the CoNiFeCu/Cu nanowires in polycarbonate templates, when relaxation periods were added after each layer deposition. Although, the resistance did not change in time, the GMR shape was still noisy.

Figure 4.3.8 CoNiFeCu/Cu nanowires in PC membranes (100 nm pores) Potentiostatic (CoNiFe@ -2 V)/Relax (×10^-7 A)/Potentiostatic (Cu @ -0.5 V)/Relax (×10^-7 A)
The anomalous codeposition of the iron group elements could also hinder the GMR results. The least noble element (Fe) forms a stable absorbed intermediate that limits the available area for Co and Ni to deposit. As a result, Fe tends to inhibit the Ni and Co deposition, possibly damaging the magnetic results. To reduce the complexities of the multilayers electrodeposition, the Fe component was removed from the electrolyte, while all the other components were kept intact.

Figure 4.3.9 shows the Fe effect on the GMR measurements, for two samples deposited of identical conditions, in 50 nm PC membranes, using double potentiostatic electrodeposition: Cu layer (-0.5 V) for 14 sec / CoNi layer (-2 V) for 1sec. The sample containing Fe shows greater resistance variance in time compared to the one without Fe. Even without Fe, all the samples electrodeposited in PC membranes showed asymmetrical, noisy time-dependent GMR behavior. Clearly the PC membrane irregularities and defects contributed to the loss of magnetic properties. Since all the GMR results obtained using polycarbonate membranes were unsatisfactory, a different kind of template was tested for making magnetic nanowires.
4.3.2.2 CoNi(Fe)/Cu Nanowires in AAO

Aluminum oxide templates (AAO) were also employed for electrodeposition support. Figure 4.3.10 shows an AFM image of the commercial available Anopore membranes used in our experiments. A honeycomb arrangement, characterized by a closed-packing array of cylindrical hexagonal cells could be observed. Varying the aluminum oxide anodizing conditions, the template’s pore diameter and spacing could be controlled. The pores diameter can vary from tens to hundreds of nanometers. Both the spacing between pores and pore diameters showed accuracy and better definition in AAO compared to the PC membranes.

For magnetic nanowires, the smallest commercial available AAO pores (20 nm diameter) were used for electrodeposition. Table 4-3-3 shows the CoNiCu bath used for making layered nanowires in AAO templates. The new bath consists of the initial electrolyte from which the Fe component and the sodium saccharin were removed.
Multilayered CoNiCu/Cu nanowires in AAO membranes were electrodeposited using alternative potentials steps. The Cu layer was controlled at (~0.325 V) and the CoNi layer was deposited at (~1.9 V). The Cu layer thickness was adjusted by varying the time of Cu deposition potential, while the alloy layer thickness was kept the same. The TEM analysis shows that a potential of (~0.325 V for 15 s) would yield a Cu layer thickness of 10 nm, while a potential of (~1.9 V for 1 s) would yield the same CoNi layer thickness. From TEM verification, the Cu current efficiency was determined to be 24 %, while the CoNi current efficiency was calculated to be 31 %.

Figure 4.3.11 shows the Cu layer thickness influence on the GMR obtained using the 20 nm pore AAO membranes. The GMR showed a maximum of 15 % at room temperature for a Cu layer of (17 s) deposition. When the Cu layer thickness was slightly increased by a longer deposition time (20 s), the GMR decreased drastically to 5 %. The GMR also decreased to 8 % when the Cu layer thinner (15 s deposition). A thicker spacer, represented by the nonmagnetic Cu layer, would make it harder for the magnetic CoNi alternating layers to sense each other and spin-couple, damaging the GMR effect. When the Cu spacer is too thin, the GMR effect would also suffer either due to non-discrete layering or from a lower number of coupled layers.

### Table 4-3-3 CoNiCu electrolyte

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSO₄</td>
<td>50</td>
</tr>
<tr>
<td>NiSO₄</td>
<td>57</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Additives</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-K Tartrate</td>
<td>27</td>
</tr>
<tr>
<td>Sulfamic Acid</td>
<td>10</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Figure 4.3.11  CoNi/Cu nanowires GMR in AAO (room temperature)

Figure 4.3.12  Cu Layer thickness influence on GMR
Figure 4.3.13 shows the GMR result when both the magnetic layers and the Cu spacer deposition times were doubled. Surprisingly, the GMR effect did not disappear, but was substantially lower.

![GMR% vs Magnetic Field (T) for CoNiCu/Cu layers nanowire](image)

**Figure 4.3.13 Thicker CoNiCu/Cu layers nanowire GMR**

In addition to the nonmagnetic layer thickness, it was observed that electrolyte additives could also influence the GMR performance. Sodium saccharin, used for reducing deposited material internal stress, proved to have a negative effect on the nanowires magnetic properties.

Figure 4.3.14 compares nanowires samples with/without saccharin. It is clear that multilayered CoNiCu/Cu nanowires plated using identical conditions [CoNiCu (1sec)/Cu (15sec)] 2400, showed irregular GMR behavior when saccharin was present in the electrolyte.

Sulfamic acid, an additive used for pH control during electrodeposition, was also tested to examine its influence on the nanowires GMR. Figure 4.3.15 shows that the sulfamic acid did not harm nor improve nanowires GMR properties.
Figure 4.3.14 Sodium saccharin effect on CoNiCu/Cu nanowire GMR

Figure 4.3.15 Sulfamic acid effect on CoNiCu/Cu nanowires GMR
The Na-K tartrate, the electrolyte complexing agent, was shown to influence the GMR behavior of the CoNiCu/Cu nanowires. When tartrate was included in the electrolyte, the GMR values were larger at lower magnetic saturation fields, Figure 4.3.16, compared to the case when the tartrate was removed from the electrolyte.

Another variable that proved to influence the nanowires GMR property was the bilayer number in the nanowires. Figures 4.3.17 (a, b) show the layer number influence the GMR: the larger the number of layers the higher the GMR.

Figure 4.3.16 Na-K Tartrate influence on GMR
Galvanostatic pulsing multilayer CoNiCu (-0.012A)/Cu (-0.001A) nanowires

The Na-K tartrate, the electrolyte complexing agent, was shown to influence the GMR behavior of the CoNiCu/Cu nanowires. When tartrate was included in the electrolyte, the GMR values were larger at lower magnetic saturation fields, Figure 4.3.16, compared to the case when the tartrate was removed from the electrolyte.

Another variable that proved to influence the nanowires GMR property was the bilayer number in the nanowires. Figures 4.3.17 (a, b) show the layer number influence the GMR: the larger the number of layers the higher the GMR.
Plotting the GMR as a function of CoNiCu/Cu layer number showed that the change in resistance with magnetic field increased when more layers were deposited in the nanowires.

Figure 4.3.17 Nanowires GMR % vs. CoNiCu/Cu bilayers number

Plotting the GMR as a function of CoNiCu/Cu layer number showed that the change in resistance with magnetic field increased when more layers were deposited in the nanowires.
The metal ion component concentration also influenced the GMR outcome. Figure 4.3.18 shows the GMR behavior when the Co concentration was increased in the electrolyte, and all the other components Ni and Cu were kept the same.

The GMR value decreased radically when more Co was added to the electrolyte. On the other hand, the GMR magnetic saturation fields decreased with the increased Co concentration. For the smallest Co concentration (1X or 50 nm CoSO₄) the GMR saturated at 3500 Oe, and decreased to 2500 Oe when the Co concentrated was 3X. The smallest saturation field of 1500 Oe was observed for the highest Co concentration (4X) scenario. A representation of Co content
influence on the GMR and the magnetic saturation field is shown in Figure 4.3.19.

![Graph](image)

**Figure 4.3.19 GMR% and magnetic field saturation function of Co content**

The Ni content in the electrolyte also seemed to influence the nanowire GMR and the magnetic saturation field. Figure 4.3.20 shows the GMR behavior for different Ni concentrations in the electrolyte. Taking as a basis Ni 1X, which was equivalent to 6 mM NiSO$_4$, the Ni concentration was increased in the electrolyte while the other components Co and Cu were kept unchanged. Higher Ni content appeared to increase the GMR value. Alternatively, lower Ni concentration seemed to decrease the GMR saturation field as Figure 4.3.21 shows.
Figure 4.3.20 Ni concentration influence on the CoNiCu/Cu nanowires
Potentiostatic pulsed multilayer nanowires
CoNiCu (-1.9 V)/Cu (-0.325V)

Figure 4.3.21 GMR% and magnetic field saturation function of Ni content
Using the conditions of the CoNiCu/Cu sample that demonstrated the best GMR, FeSO$_4$ was added to the electrolyte to obtain CoNiFeCu/Cu multilayered nanowires. Figure 4.3.22 shows that adding Fe to the CoNiCu electrolyte reduced the GMR effect. Other samples were attempted using higher or lower FeSO$_4$ concentration in the electrolyte. Figure 4.3.22 shows the nanowires GMR behavior for different amounts of FeSO$_4$ present in the electrolyte. When more FeSO$_4$ (16 mM) was introduced in the electrolytic bath, the nanowire resistance displayed high variation in time, in contrast to the lower Fe concentration case (1.8 mM) that demonstrated a low GMR but no resistance time dependence. When Fe was totally removed from the bath, the resistance was constant in time and the GMR value increased drastically.

![Figure 4.3.22 Fe content influence on nanowires GMR %](image_url)

Figure 4.3.22 Fe content influence on nanowires GMR %

The nanowires GMR profile showed an interesting behavior upon measurement. When a nanowire sample was first exposed to a magnetic field its initial resistance drop is the largest.
This behavior is also known as the “virgin state GMR”. Figure 4.3.23 shows a typical case of GMR change from the virgin state to the “trained” state. After the first applied magnetic field, the resistance drop (GMR %) settles down to a lower value (the trained state) that does not change with the number for measurements or re-runs. In all the previous figures shown in this chapter the “trained” (lower GMR) state was reported.
CHAPTER V NANOTUBE ELECTRODEPOSITION RESULTS AND DISCUSSION

Recently, electrodeposition inside nanoporous membranes has been investigated as a feasible method for obtaining nanometric size wires. However, nanotubes electrodeposited inside porous membranes have not yet been fully explored. Nanometric, magnetic tubes may be of interest for both advanced catalytic and sensory materials, as well as magnetic field sources for nanoelectromechanical devices.(Y.C. Sui, 2004) In addition, corrosion resistant nanotubes, such as NiCoCu materials, may be possible materials as transport vessels for nanoparticles (Vankrunkelsven, 2004), bioseparations (S. Hou, 2004) and components of novel core-shell cable alloys (W-C.Yoo, 2004). Gold tubular-like shapes were reported by Kautek, et al. (Kautek, 1995) in a study of Au nanowire electrodeposition. When the back of the membrane pores was not fully sealed by an initial sputtering step, nanowires were not formed and short tubular-like structures observed. In addition, short 1 m nanotubes were observed by Vaidyanathan et al. (Vaidyanathan, 2003) in the underpotential deposition of In$_2$Se$_3$ semiconductors. The Martin group demonstrated more robust Au nanotubes in polycarbonate and alumina templates by electroless deposition (Martin, 1994, 2001). They were also successful in using a sol-gel method for the deposition of silica nanotubes (Miller, 2001), test tubes (Gasparc, 2004), a wide variety of semiconductor oxides (Lakshmi, 1997) and polypyrrole (Yamada, 2004) inside alumina templates.

Our study explores the fabrication of nanotubes by electrodeposition in nanoporous templates. In contrast to the electroless and sol-gel methods, the electrodeposition technique may find a niche in the control of alloy composition. To demonstrate the concept, CoNiCu alloys are electrodeposited as tubes into polycarbonate films with non-conducting walls, and into Anopore aluminum oxide (AAO) templates. The metal reaction is accompanied by gas-evolving side
reactions that contribute to the tube formation. Both polycarbonate (PC) Millipore Isopore™ membrane filters, with specified pore diameters of 800 nm and pore length of 10 m, and Anopore Aluminum Oxide (AAO) membranes, with specified pore diameters of 200 nm and pore length of 60 m, were used as mediums for nanotubes synthesis. For electrical contact, gold was sputtered on one side of the membrane. The gold sputtering time was varied as listed in Table 5-1. A three-electrode cell setup was used, as described in Chapter 3. The electrolyte for nanotube deposition was composed of 50 mM CoSO₄, 18 mM NiSO₄, 1 mM CuSO₄, 27 mM potassium tartrate, 10 mM sulfamic acid, 4 mM sodium saccharin, and 0.6 g/L Triton X-100. The CoNiCu alloy electrodeposition was carried out at constant potential of –1 V vs. SCE. Copper was deposited from the same CoNiCu electrolyte, but at a more noble potential, -0.325V. A concentrated copper sulfate bath of high current efficiency ~100% (Dinan, 1991, Chene and Landolt, 1989) (0.4M CuSO₄, 0.5M H₂SO₄) was also used to probe the influence of the side reactions in the porous membranes electrodeposition.

5.1 Nanotubes in PC Membranes

Table 5-1 summarizes the experimental conditions used for fabricating the nanomaterials. The effect of the Au sputtering time on the underside of the membranes was investigated. All plating parameters were kept constant, -1 V deposition for 60 min, while the gold sputtering time increased from 20, 30 to 50 min. Tubes were observed by SEM for substrates with Au sputtering times of 20-50 min. Figure 5.1(a)-(c) shows SEM micrographs of the CoNiCu tubes in the different sputtered substrates. A decrease in the tube wall thickness with increased sputtering time was observed. In Figure 5.1(a) the PC membrane was sputtered for 20 min and the observed tube wall thickness averaged 155 nm with 35 nm standard deviation. The array of tubes was also sparse.
When the PC membrane sputtering time was increased to 30 min, the nanotube wall thickness averaged 132 nm with 15.7 nm standard deviation, Figure 5.1(b). The total charge passed, determined by integrating the current, was −2.75 and −2.43 C for the two Au sputtering times of 20 and 30 min, respectively. An even longer Au membrane sputtering time of 50 min resulted in a deposit with a thinner tube wall thickness of 68 nm and 26.8 nm standard deviation, and a more dense tube population. Also, when the membrane sputtering time increased, the tubes grew taller. The charge passed was −5.64 C, larger than the short Au sputtering time samples, which is consistent with a larger reactive area for the constant deposition time. A qualitative EDS analysis in Figure 5.1(d) indicates the presence of CoNiFe and a quantitative XRF analysis found the composition to be: 48-wt % Co, 38-wt% Cu and 14-wt% Ni. As indicated in Table 5.1, Cu tubes were also obtained from the CoNiCu electrolyte at −0.325 V. For this case the electrodeposition time was increased to compensate for the lower current density and the membrane was sputtered for 50 min.
Figure 5.1. SEM Micrographs of CoNiCu Nanotubes electrodeposited at constant potential of -1V for 60 min from CoNiCu electrolyte: (a) 20 (b) 30 (c) 50 min sputtering time. EDS spectrum (lower right)
Figure 5.2 shows the SEM micrographs of the Cu nanotubes plated from the CoNiCu bath, which is expected to have an efficiency of less than 50 % due to its low electrolyte concentration. Nanotubes of approximately 5 m length were observed, while the wall thickness averaged 218 nm. The EDS analysis in Figure 5.2 shows a deposit of pure Cu, also confirmed by XRF. Figure 5.3 (a)-(b) shows the PC membrane underside after gold sputtering at (a) 10 min and (b) 50 min. In both cases the sputtering did not seal the membrane pores. The preferential plating at the inner wall can be attributed to a small amount of Au sputtered around the edge of the pores, but it doesn’t completely explain why the tubes do not deposit axially to create wires. Since the CoNiCu electrolyte used here has been reported to have current efficiencies less than 50 % for both alloy and Cu deposition, it was suspected that the resulting gas evolution also contributed to the formation of the nanotubes. To further inspect the role of the side reaction, a high efficiency Cu electrolyte was used with a deposition potential of -0.325 V, see Table 5.1. A shortly sputtered membrane of 10 min was used. After 150 min of deposition time, Cu wires were obtained instead of tubes, Figure 5.4). The wire length was 6 m. Chene and Landolt reported a 100% current efficiency for this concentrated Cu electrolyte used here resulting in nanowires, while Huang et al. (Huang, 2002, Huang and Podlaha, 2004) reported a value of 45 % for Cu deposition from a similar electrolyte used to deposit the nanotubes in Figure 5.2. Thus, gas evolution plays a significant role in the formation of nanotubes. When there is no gas generation, as in the concentrated Cu electrolyte, nanowires were obtained instead of tubes. A suggested mechanism is that for horizontally positioned membranes, the generated H2 finds a path from the growing electrode surface through the pore center to the pore mouth, and subsequently blocks the deposition in its path.
Examining the versatility of the tube-wire formation, core-shell structures were fabricated. Conditions of deposition are given in Table 5-1. The CoNiCu nanotubes were first electrodeposited at -1V for 60 min from the CoNiCu solution with a membrane sputtered with gold for 20 min.

Figure 5.2 SEM micrograph of Cu nanotubes plated from the CoNiCu bath at –0.325V Cu EDS spectrum (lower right).
After making the CoNiCu tubes, the center area was filled by electrodepositing Cu from the concentrated Cu electrolyte at –0.325 V. Figure 5.5 confirms the wire architecture. The EDS spectrum in Figure 5.4 indicates a significantly larger Cu peak compared to Figure 5.1 in the CoNiCu alloy, as expected from the increased Cu in the core. The XRF analysis confirms the increased Cu content in the core-shell wire: 25.7 wt% Co, 49.7 wt% Cu, and 24.6 wt% Ni.

Figure 5.3 Different Au sputtering times of the PC membranes: (a) 15 and (b) 50-min.
Figure 5.4 Cu nanowires SEM micrograph: same sample: a) lower b) higher magnification
5.2 Nanotubes in AAO Membranes

Using the same electrolyte, aluminum oxide templates with (200 nm) pores were used for fabricating multilayered CoNi/Cu nanotubes. Cyclic voltammetry at various scan rates was applied to characterize the CoNiCu electrolyte. Figure 5.6 shows the current response for different sweep rates in potential. The faster sweep rates simulate the non-steady state processes during the tube electrodeposition. In the cyclic voltammetry plot, Figure 5.6 (a), the peaks represent the diffusion-controlled species. The linear dependence of the Cu peak currents on the square root of sweep rates shows that Cu is under diffusion control, as expected. In Figure 5.6 (b) the current density reflects the real plating area (0.02 cm²) and the potential was also corrected for ohmic drop (29 ohms).

Figure 5.5 SEM micrograph of core-shell wires; inset: EDS spectrum.
Figure 5.6 Cyclic Voltammetry of CoNiCu at Different Sweep Rates
(a) expanded scale (b) Copper deposition region
The Cu peak current increases with faster sweeps in potential, typical behavior in diffusion controlled reactions. The other peak in Figure 5.6 (a) signifies that there is a diffusion-controlled reaction in the region where CoNiCu deposits, at high negative potentials -2.5 V.

Using potentiostatic pulsing (-0.4 V Cu layer/-1.7 V CoNi layer), CoNi/Cu nanotubes were electrodeposited in AAO membranes. Figure 5.7 shows nanotubes SEM micrographs.

![Figure 5.7 SEM micrograph of CoNiCu nanotubes in AAO membranes](image)

The tube outer diameters were observed to be approximately 300 nm, larger than the manufacturer specifications (200 nm). However, these AAO tube diameters are smaller than the PC nanotubes (1 μm diameter). For this reason, the SEM micrographs are not as clear as the larger tubes formed with the PC membrane. TEM was used for higher resolution imaging of
these narrow tubes. Figure 5.8 shows a micrograph of CoNi/Cu tubes in AAO template, electroplated using potentiostatic pulsing: (-0.325 V Cu layer/ -2 V CoNi layer). Although the layers were not visible, crystal grains, having a size of about 80 nm, were distinguished. Under TEM examination tubular structures were clearly seen, as evidenced by the darker regions that represent the thicker 2D tube projection of the wall, while the lighter regions indicate the hollow, annular region of the tube. A different sample of nanotubes was electrodeposited using longer layer deposition times, in order to make thicker layers that would be distinguishable at the TEM.

Figure 5.8 TEM of CoNi/Cu nanotubes obtained from short plated layers

Figure 5.9 (a) and (b) show a CoNi/Cu nanotube obtained using longer electroplated layers: Cu Layer (-0.325 V for 200 s) / CoNi Layer (-2 V for 5 s). At lower magnification, Figure 5.9 (a), the tube looks more defined, dense, having thicker walls. At the highest magnification, Figure 5.9 (b), the nanotubes layers were visible but not very clear, as indicated by the arrows. The Cu layer was estimated to be around 3.5 nm, while the CoNi layer was 2 nm thick. A higher resolution TEM would be needed to image thinner layers in nanotubes.
Figure 5.9 CoNi/Cu multilayered tubes (a) low magnification (b) high magnification (layers) 
(Cu layer -0.325 V for 200 s) / (CoNi layer -2 V for 5 s)
5.3 AAO Nanotube Magnetic Properties

The magnetic properties of the CoNiCu alloy nanotubes, plated at constant potential of –1.9 V in AAO membranes, were examined. After electrodeposition the sample magnetization was measured in plane and perpendicular to the tube plane. The sample showed magnetic anisotropy, with a magnetization easy axis along the tubes axis. Figure 5.10 shows the CoNiCu alloy nanotube BH loops. The tubes showed a rather small coercivity of 150 Oe for both parallel and perpendicular measurements. When the magnetic field was directed perpendicular (along the tubes axis) the BH loop showed enhanced squareness, and lower saturation field.

The GMR effect was tested on the multilayered CoNi/Cu nanotubes. The nanotubes were not grown all the way to the top of the AAO membrane in order to prevent the filling of the tubes.
For electrical contacts, the AAO membrane was partially dissolved. Figure 5.11 shows the GMR curve of a multilayered tube sample obtained by electrodeposition in AAO membrane using a double potentiostatic scheme: Cu layer (-0.325 V for 80 s) / CoNi layer (-2 V for 2 s). The GMR saturation field was approximately 0.3 T. The nanotubes GMR for several re-runs settled at around 3.5 % at room temperature. The virgin state showed much larger GMR (8.2 %), but it was observed only on the first measurement.

Figure 5.12 shows the GMR of a nanotubes sample plated at identical conditions to the pervious sample, changing only the electrolyte pH to a lower value of 2, half the previous sample pH. The change in pH seemed to influence the nanotubes GMR. At natural pH shown (Figure 5.11), the GMR was much higher than the GMR obtained from the acidic electrolyte shown in Figure 5.12.
However, the saturation in magnetic field for the acidic bath was slightly lower (0.2 T) than the normal pH saturation field (0.3 T). Figure 5.13 shows the GMR of a CoNi/Cu nanotube array plated at a higher Cu potential and a lower alloy potential: Cu Layer (-0.4 V) / CoNi Layer (-1.7 V) (natural pH = 4). The sample showed ~ 2.7 % GMR at low magnetic field (0.2 T). Although this GMR value is not as high the one presented in Figure 5.11, it has lower magnetic field saturation. The inset in Figure 5.13 is a TEM micrograph of the tubular architecture.

Figure 5.14 shows the CoNi/Cu tube GMR when the alloy deposition potential was lowered to -1.5 V, using the natural pH = 4 bath. The GMR value is higher (3.5 %), but the magnetic saturation field is also higher, 0.5 T.

Figure 5.12 GMR plot of multilayer CoNi/Cu tubes (acidic pH = 2)
Figure 5.13 Multilayer CoNi/Cu tubes GMR (Cu layer –0.4 V/CoNi layer -1.7 V)

Figure 5.14 Multilayer CoNi/Cu tubes GMR (Cu layer –0.4 V/CoNi layer -1.5 V)
Adding small quantities of Fe (1 mM) to the CoNiCu electrolyte, tubes were obtained and their GMR was measured. Figure 5.15 shows the GMR curve of the CoNiCuFe/Cu multilayered nanotubes. The change in resistance is 2.5% (trained state) at (0.4T) magnetic saturation field. The sample shown in Figure 5.15 was plated at higher negative Cu potentials (-0.55 V) and also higher alloy potential (-2.2 V).

![GMR Curve](image)

Figure 5.15 Multilayer CoNiFe/Cu tubes GMR (Cu layer –0.55 V/ CoNiFe layer -2.2 V)

Removing the Na-K tartrate from the bath destroyed the GMR behavior for the conditions stated in Figure 5.15. TEM examination of the sample plated from the bath without tartrate showed dark clusters inside the tubes, which may indicate the presence of precipitation products accumulating inside the tube, Figure 5.16.

![TEM Image](image)

Figure 5.16 CoNi/Cu tubes of undesirable GMR: (Cu -0.55 V/ CoNi -2.2 V) without Na-K tartrate
CHAPTER VI CONCLUSIONS

An experimental study was conducted to explore the electrodepositing of the FeCoNiCu quaternary system into multilayered nanowires and tubes. Compositionally modulated multilayers of (Fe)CoNiCu/Cu were obtained using double potentiostatic/galvanostatic pulse schemes. Other variations in the deposition procedure included combined potentiostatic and galvanostatic pulses and the introduction of relaxation periods after each pulse. The Cu deposition potential was between (–0.3 V and -0.5 V); the Co-rich alloy deposition potentials were between (–1.5 V and –2.3 V). Several different membrane pore sizes were used to electroplate the nanowires. The PC membranes showed major irregularities and defects, which affected the nanowires magnetic properties. The anodic aluminum oxide membranes were found to have better definition and to yield more reliable magnetic results. Both Cu and Co-rich alloy nanowires were fabricated under potentiostatic control deposition.

The nanowire GMR measurements demonstrated that the GMR effect is dependent on electrolyte components, additives and pH. Also, the number of layers electroplated in the nanowires showed to influence the GMR value: the higher the layer number, the higher the GMR. The nonmagnetic layer (Cu) thickness also had an effect on the resistance change in magnetic field. The highest GMR (15 %) at room temperature was observed for the CoNi/Cu multilayered nanowires with 2400 bilayers, deposited inside AAO membrane. The GMR magnetic field saturation for the multilayered nanowires was quite low, under 0.5 T, which would make these nanostructures excellent sensor materials. Magnetic anisotropy was observed for Co-rich alloy nanowires with an easy axis along the wire axis.

Electrodeposition was used to grow metallic CoNiCu and Cu nanotubes in polycarbonate membranes and aluminum oxide templates. It is the first time CoNiCu nanotubes were reported
and the very first demonstration of a nanotube exhibiting GMR. The tube wall thickness was controlled by electrodeposition. The tubes were obtained from a low efficiency CoNiCu electrolyte, critical to the evolution of tubes formation. Several micron long electrodeposited CoNiCu and Cu nanotubes were reported. Tube formation was attributed to the H₂ generation from the side reactions. Different sputtering times affected the density of tubes and their shape. Core-shell nanowires were obtained by filling the CoNiCu nanotubes with Cu from the concentrated CuSO₄ bath.

The nanometric layer sizes were well controlled by electrodeposition. As compared with vapor processes, electrodeposited multilayers have a less sharp composition interface due to the inherent non-steady state pulsed electrodeposition. However, electrodeposition is one of the few methods that can overcome the geometrical restrictions of inserting metal into very deep nanometric recesses, making it the number one method for making nanowires and nanotubes.
REFERENCES


APPENDIX CALCULATIONS

Definitions and Constants

- \( \text{unicharge} := 1 \quad \text{equiv} := \text{unichargemol} \quad \mu m := 10^{-6}m \)
- \( n := 2 \cdot \frac{\text{mol}}{\text{equiv}} \quad \text{Faraday} := 96485 \cdot \frac{\text{coul}}{\text{equiv}} \quad \text{nm} := 10^{-9}m \)

Cu Layer Calculation

Estimate the amount of Cu platting by applying Faraday's law:

\[
\frac{I}{n \cdot \text{Faraday}} = \frac{m_{\text{Cu}}}{\text{MW} \cdot t}
\]

where

- \( I = \) current applied
- \( n = \) number of electrons
- \( F = \) Faraday's constant
- \( \epsilon = \) efficiency factor
- \( m = \) mass plated
- \( \text{MW} = \) molecular weight
- \( t = \) time plated

- Estimate the volume to be plated
  (filling 6 micron deep size holes, 50 nm pore diameter):

\[
D := 50 \text{nm} \quad L := 6 \mu m \quad \rho_{\text{Cu}} := 8.94 \cdot \frac{\text{gm}}{\text{cm}^3} \quad V_{\text{Cu}} := L \cdot \pi \cdot \left( \frac{D}{2} \right)^2
\]

\[
V_{\text{Cu}} = 1.178 \times 10^{-14} \text{cm}^3
\]

The mass of copper plated in one nanowire can be expressed as:

\[
M_{\text{Cu}} := V_{\text{Cu}} \cdot \rho_{\text{Cu}}
\]

\[
M_{\text{Cu}} = 1.053 \times 10^{-13} \text{gm}
\]

- Calculate the number of nanowires to be plated:

Electrode Exposed Area

\( A_{\text{exposed}} := 2.25 \cdot \text{cm}^2 \)

Given Pore Density

\( \text{poredensity} := 4 \cdot 10^8 \cdot \frac{1}{\text{cm}^2} \)
Number of nanowires

\[ N_p := A_{\text{exposed}} \cdot \text{poredensity} \quad N_p = 9 \times 10^8 \]

Pore area

\[ A_p := \pi \cdot \left( \frac{D}{2} \right)^2 \quad A_p = 1.963 \times 10^{-11} \text{ cm}^2 \]

Real Plated Area

\[ A_{\text{plated}} := A_p \cdot N_p \quad A_{\text{plated}} = 0.018 \text{ cm}^2 \]

The time to fully grow Cu nanowires can be calculated using:

- Experimental observed current
  \[ I_Cu := 8.5 \times 10^{-5} \text{ A} \]
- Assuming efficiency(100%)
  \[ \varepsilon_{\text{Cu}} := 1 \]
- Calculated Cu mass plated in all nanowires
  \[ m_{\text{Cu}} := M_{\text{Cu}} \cdot N_p \]

\[ MW_{\text{Cu}} := 63.54 \frac{\text{gm}}{\text{mol}} \quad t_{\text{Cu}} := \frac{m_{\text{Cu}} \cdot \text{n-Faraday}}{I_{\text{Cu}} \cdot MW_{\text{Cu}} \cdot \varepsilon_{\text{Cu}}} \quad t_{\text{Cu}} = 3.387 \times 10^3 \text{ s} \]

**Alloy (Co) Layer Calculation**

Estimate the amount of Co plating by applying Faraday's law:

\[ V_{\text{Co}} := L \cdot \pi \cdot \left( \frac{D}{2} \right)^2 \quad \frac{I}{n\cdot\text{Faraday}} = \frac{m_{\text{Co}}}{MW \cdot t} \]

\[ V_{\text{Co}} = 1.178 \times 10^{-14} \text{ cm}^3 \]

The mass of Co plated in one nanowire can be expressed as:

\[ \rho_{\text{Co}} := 8.92 \frac{\text{gm}}{\text{cm}^3} \quad M_{\text{Co}} := V_{\text{Co}} \cdot \rho_{\text{Co}} \]

\[ MW_{\text{Co}} := 58.9 \frac{\text{gm}}{\text{mol}} \quad M_{\text{Co}} = 1.051 \times 10^{-13} \text{ gm} \]
The time to fully grow Co nanowires can be calculated using:

Experimental observed current \( I_{Co} := 10.5 \cdot 10^{-3} \text{ A} \)

Assuming efficiency(100%) \( \varepsilon_{Co} := 1 \)

Calculated Co mass plated in all nanowires \( m_{Co} := M_{Co} \cdot Np \)

The time to fully grow Co only nanowires can be calculated:

\[
t_{Co} := \frac{m_{Co} \cdot n \cdot \text{Faraday}}{I_{Co} \cdot M_{Co} \cdot \varepsilon_{Co}}
\]

\( t_{Co} = 29.51 \text{ s} \)

**Efficiency Calculations**

Different experiments were performed to observed the actual time it takes to fill up the membrane with either Cu or Co (alloy).

\( t_{observedCu} := 4500 \cdot \text{sec} \)

\( t_{observedCo} := 700 \cdot \text{sec} \)

\( t_{Cu} = 3.387 \times 10^3 \text{ s} \) (calculated above by Faraday's Law)

\( t_{Co} = 29.51 \text{ s} \)

\[ \varepsilon_{Cu} := \frac{t_{Cu}}{t_{observedCu}} \]

\( \varepsilon_{Cu} = 0.753 \)

\[ \varepsilon_{Co} := \frac{t_{Co}}{t_{observedCo}} \]

\( \varepsilon_{Co} = 0.042 \)
Bi-Layers Calculations

- Time to plate 10nm thick Co layer can be calculated using efficiency

\[ \text{Layer}_\text{Co} := 10\text{nm} \quad t_{\text{layerCo}} := \frac{\left( \frac{\text{Layer}_\text{Co} \cdot t_{\text{Co}}}{L} \right)}{\varepsilon_{\text{Co}}} \quad t_{\text{layerCo}} = 1.167\text{s} \]

- The time to plate 10nm thick Cu layers:

\[ \text{Layer}_\text{Cu} := 10\text{nm} \quad t_{\text{layerCu}} := \frac{\left( \frac{\text{Layer}_\text{Cu} \cdot t_{\text{Cu}}}{L} \right)}{\varepsilon_{\text{Cu}}} \quad t_{\text{layerCu}} = 7.5\text{s} \]

- BiCycles Calculations:

\[
\text{cycle} := t_{\text{layerCu}} + t_{\text{layerCo}} \quad \text{cycle} = 8.667\text{s}
\]

\[
N_{\text{cycle}} := \frac{8000 \cdot \text{s}}{\text{cycle}} \quad N_{\text{cycle}} = 923.077 \quad \text{(bicycles)}
\]

Table A  Flat Plate Deposition XRF Analysis

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<th>NI wt%</th>
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<td>3.78E-03</td>
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Table B  Partial Current and Efficiency Calculation
VITA

Mrs. Despina Mehedintu Davis was born in March 1978 in Ploiesti, World War II oil center in central Europe, Romania. She came to USA for her bachelor degree and graduated in May 2002 from Texas Tech University with a dual degree in chemical engineering and chemistry. In the fall of 2002, she came to Louisiana State University where she enrolled in the graduate studies in the department of Chemical Engineering. The Master of Science degree in Chemical Engineering will be conferred in May 2005, and she continues working on a doctoral degree in the engineering department. A list of publications and presentations include:


iv. D. Davis and E.J. Podlaha, “CoFeNiCu/Cu Nanowires and Tubes”, 205th Meeting of the Electrochemical Society, San Antonio, TX, May 9, 2004


