Electrodeposition of Fe-Ni-Co, and Cu Thin Films, Nanowires, and Sculpting Nanoscaled Features

A Dissertation Presented
By
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to
The Department of Chemical Engineering

In partial fulfill of the requirements
For the degree of

Doctor of Philosophy

In the field of

Chemical Engineering

Northeastern University
Boston, Massachusetts

April 20, 2017
ACKNOWLEDGEMENT

I would like to thank my advisor Professor Elizabeth J. Podlaha for her support and encouragement. I thank her for teaching me first-hand laboratory techniques and underlying theory, for her patience in discussions during experiments, and for her strong work ethic, which pushes me to excel in my interests and work hard to achieve my goals.

I would like to thank my committee members, Professor Katherine S. Ziemer, Professor Sunho Choi, from Department of Chemical Engineering at Northeastern University and Professor Sunggook Park from Department of Mechanical Engineering at Louisiana State University for their guidance and help during my PhD study. I want to thank my labmates, Deyang Li, Yujia Zhang, Cheng Wang, Ahmed Sajjad, for their help and company. I thank laboratory alumni: Dr. Salem Zahmi for his instruction about class homework, Dr. Shaopeng Sun, Dr. Avinash Kola, Usoa Izagirre Etxeberria, Yanping Cui, Kimberley Duarte, Matthew Silva, Anh Phong Tran, and Eric Navarrete for their help and company.

I also would also like to thank Mr. William Fowle and Dr. Wentao Liang for
help with FESEM, HRTEM training, and Mr. Robert Eagan for machining help.

Lastly, I would like to thank Roche Diagnostics and the US National Institutes of Health (NIH) for the financial support of my project.
ABSTRACT

Nanogap electrodes are elements of nanoscale microfluidic devices and sensors, and have been prepared by different techniques. The presented idea is to build a pair of nanogap electrodes using novel nanowire-electrodeposition approaches. The nanogap electrodes, or the precursor nanowires are to be aligned with a nanogap size of < 10 nm, required for molecular sensing, and exhibit high electronic conductivity, corrosion resistance, thermal stability, scalable productivity, and most important be economically viable.

To meet the above requirements, two strategies were invented. In the first methodology, Fe-Ni-Co nanotips at the end of nanowires were fabricated at the interface of two Fe-Ni-Co regions via a combination of pulse electrodeposition, anodization and chemical etching. The wires were fabricated with three, consecutive electrochemical conditions, where first an Fe-Ni-Co wire segment was deposited, followed by an anodic potential to induce growth of an iron oxide thin film, and then followed by an applied, pulse cathodic current density to reduce the oxide and deposit another layer of Fe-Ni-Co. Upon etching, tips formed at the end of the last Fe-Ni-Co
region, as evidenced by SEM. Potential transients during the last applied cathodic pulse current step, suggests that both the reduction of the oxide and metal occur, and that TEM/SAED confirm changes in the crystalline Fe-Ni-Co structure at the interfacial region between steps that contributes to the tip formation.

In the second methodology, Fe-Ni-Co nanowires with a thinned nanowire segment are created utilizing template-assisted electrodeposition, and a coupled displacement reaction with a more noble elemental ion, Cu(II), and at the same time dealloying predominantly Fe from Fe-Ni-Co by the reduction of protons (H’), followed by a subsequent etching step. The displacement/dealloyed layer is sandwiched between two Fe-Ni-Co segments to facilitate the fabrication of nanogaps with the assistance of a nano-sized channel and future connection with external facilities.

The behavior and effective predominate parameters during coupled displacement/dealloying reactions into Fe-Ni-Co nanowires in the axial direction was studied. The penetration length rate was found to be a function of the ratio of proton and Cu(II) concentration, and a ratio of 0.5 was found to provide the largest
penetration rate, and hence the larger thinned length of the nanowire. Altering the etching time affected the diameter of the thinned region. This methodology presents a new way to thin nanowire segments connected to larger nanowire sections, and also introduces a way to study the propagation of a reaction front into a nanowire. The methodology was also applied to Mo-alloys to create novel Cu-Mo-Ni-Fe nanowires.

A Kinetic Monte Carlo (KMC) simulation was applied to investigate the metal ion penetration and porous structure evolution. Simulation results predict that reconstruction of the local porous structure during etching was one of the main reasons that etching of Cu-Fe-Ni-Co nanowires leads to a thinning effect without vacancy induced breakage. An optimized percentage range for the remaining Fe, Ni atoms was identified, where the porous, Cu-Fe-Ni alloy can be thinned uniformly.

Finally, a thin and uniform gold layer was successfully coated on the as-prepared multi-diameter Fe-Ni-Co/Cu-Fe-Ni-Co nanowires through gold electroless deposition with the purpose of increasing conductivity and corrosion resistance. SEM-EDS mapping results indicate a uniform distribution of the deposited gold element along the whole nanowire.
TABLE OF CONTENTS

LIST OF FIGURES ......................................................................................................................... ix
LIST OF TABLES ............................................................................................................................... xv

1 INTRODUCTION ............................................................................................................................. 1

2 LITERATURE REVIEW .................................................................................................................. 6

   2.1 DNA sequencing ..................................................................................................................... 6
      2.1.1 First-generation of DNA sequencing ............................................................................. 7
      2.1.2 Second-generation of DNA sequencing ........................................................................ 9
      2.1.3 Third-generation of DNA sequencing ........................................................................... 12

   2.2 Nanogap fabrication .............................................................................................................. 13
      2.2.1 Mechanical break junctions .......................................................................................... 13
      2.2.2 Gap narrowing by electrodeposition or chemical deposition .................................. 14
      2.2.3 Electromigration ........................................................................................................... 16
      2.2.4 Focused ion beam ......................................................................................................... 18
      2.2.5 Silicon tip sharpening ................................................................................................... 20
      2.2.6 Molecular ruler ............................................................................................................. 21
      2.2.7 Template electrodeposition ......................................................................................... 23

   2.3 Electrodeposition and three electrodes system .................................................................... 26

   2.4 Sculpting nano-features with displacement and dealloying reactions ............................. 27

   2.5 Nanotip fabrication .............................................................................................................. 30

   2.6 Cu-Mo nanowires ............................................................................................................... 31

   2.7 Monte Carlo (MC) and Kinetic Monte Carlo (KMC) ......................................................... 32

3 EXPERIMENTAL .......................................................................................................................... 36

   3.1 Fe-Ni-Co nanotip .................................................................................................................. 36

   3.2 Fe-Ni-Co nanogaps with electrodeposited Cu as sacrificial layer ................................ 39
      3.2.1 RCE experiments on Fe-Ni-Co and Cu .................................................................. 40
      3.2.2 Fe-Ni-Co/Cu/Fe-Ni-Co nanowire fabrication and etching .................................. 40

   3.3 Fe-Ni-Co nanowires with thinned segments .................................................................... 42

   3.4 Cu-Mo-Iron group alloy nanowire ................................................................................... 45

   3.5 Gold coated nanowire and alignment .............................................................................. 47

4 THEORETICAL KMC MODELING ............................................................................................... 49
4.1 KMC simulation of metal ion penetration .................................................. 49
4.2 KMC simulation of Cu-Fe-Ni nanowire thinning ........................................ 55
5 RESULTS AND DISCUSSION ........................................................................... 57
  5.1 Fe-Ni-Co nanotips ..................................................................................... 57
    5.1.1 Thin film and polarization ..................................................................... 58
    5.1.2 Nanowires .......................................................................................... 64
    5.1.3 Nanotips ............................................................................................ 69
  5.2 Fe-Ni-Co nanogaps with electrodeposited Cu as sacrificial layer .............. 77
    5.2.1 RCE experiments on Fe-Ni-Co and Cu .............................................. 77
    5.2.2 Fe-Ni-Co nanogaps fabrication ......................................................... 80
  5.3 Fe-Ni-Co nanowire with thinned region ................................................... 83
    5.3.1 Parameters effect during metal ion penetration and thinning .......... 87
    5.3.2 Modeling .......................................................................................... 97
    5.3.3 Thinning ............................................................................................ 101
  5.4 Kinetic Monte Carlo (KMC) simulation .................................................... 102
    5.4.1 KMC simulation of Cu(II) penetrate into Fe-Ni nanowires .......... 102
    5.4.2 KMC simulation of nanowire thinning ............................................. 104
  5.5 Cu-Mo-Iron group alloy nanowire fabrication ......................................... 109
  5.6 Gold coated nanowire and alignment ....................................................... 115
6 CONCLUSION .................................................................................................. 120
7 RECOMMENDATIONS ..................................................................................... 124
8 NOMENCLATURE .......................................................................................... 126
9 REFERENCE ................................................................................................... 128
LIST OF FIGURES

Figure 1. Sanger’s (chain-termination) method for DNA sequencing.[20] (a) primer and DNA template, (b) primer elongation with four of the standard deoxynucleotides, terminated by dideoxynucleotides, and (c) part of radioactively labeled sequencing gel[25]. ............................................................................9

Figure 2. Illumina workflow. Starting from fragmentation and adapter ligation steps, after adhesion to a solid surface, an isothermal process is used for DNA segment amplification into a cluster. The cluster fragments are annealed with a sequencing primer and subjected to sequencing by synthesis using labeled nucleotides. A sequence is finally read out through imaging [29]. (see [30] for more details) ..............................................................................11

Figure 3. Mechanical break junction method for nanogap fabrication [44]. .................14

Figure 4. Electrodeposition and feedback system for nanogap tuning, (a) two sharp tips with a distance ranging from 200 nm to 500 nm fabricated by focused ion beam. (b) < 10 nm nanogap formed by electrodepositing metals outside of the tip; a feedback system was used to control the final gap size [45]. ....16

Figure 5. Schematic of an electromigration break-junction induced nanogap [49]. ....18

Figure 6. Illustration of focused ion beam milling substrate [52]. .....................................19

Figure 7. Schematic illustration of silicon etching for tip sharp, (a) a tip with 200 nm - 300 nm top layer before etching, (b) a nanogap prepared after etching the top layer [58]. ........................................................................................................21

Figure 8. Schematic of the scaling-down process. (a) Electron-beam lithography forms the parent structures (yellow rectangles), (b) layer-by-layer construction of metal-organic resist (2 nm per layer). The arrow represents the mercaptoalkanoic acid (tail is the SH group). (c) Metal (Blue arcs and rectangle) evaporation into the gap (the gap size is determined by the number of organic layers deposited), and (d) Lift-off of the organic layer in HCl/DMF solution [59]. ........................................................................................................23

Figure 9. Schematic of nanowire fabrication using a nanoporous membrane as a template. (a, b, c, and d) multi-segments of nanowires deposited (e and f)
liberated nanowires. (g) chemically or electrochemically etching the sacrificial layer to obtain gaps on nanowires.

Figure 10. Schematic illustration of Pd nanotube and Pt nanowires fabrication using displacement reaction with Pt nanowires [76].

Figure 11. Schematic illustration of porous structure generated by dealloying reaction.

Figure 12. Nanogap and nanotip fabrication schematic with different applied pulse current or DC potential waveforms. (a) Nanoporous template with a thin gold film layer, (b) first layer of Fe-Ni-Co was electrodeposited to partially fill the pores, (c) an anodic or OCP potential was applied to create an oxide layer, (d) a second layer of Fe-Ni-Co nanowire was electrodeposited on top of the oxide layer with the same condition as mentioned in step b, (e) the template was removed to release the nanowires, (f) nanowires were etched in a pH 5 boric-citrate solution for fabricating nanotips.

Figure 13. SEM and HRTEM used in this project.

Figure 14. Schematic for Fe-Ni-Co nanogaps fabrication with electrodeposited Cu as the sacrificial layer. (a) polycarbonate membrane was coated with a thin layer of Au by sputtering, (b) electrodeposited first layer of Fe-Ni-Co, (c) electrodeposited a short layer of Cu, (d) electrodeposited the second layer of Fe-Ni-Co, (e) release the nanowires from the membrane template, (f) electrochemically etching away Cu create the gaps.

Figure 15. Nanowire bi-segment thinning procedure. (a) procedure: electrodeposition into a gold sputtered membrane, exposure of the membrane containing the deposit structure into an acid copper solution resulting in a bi-layer structure, removal of the template, and release of the nanowires facilitated by ultrasonic agitation, followed by a selective copper etch resulting in a multi-scale diameter wire.

Figure 16. Bi-segmented Cu-Mo-iron group nanowires fabrication procedure. (a) electrodeposit Fe-Ni-Mo into a gold-sputtered membrane, (b) exposure of the membrane containing the deposit structure into an acid copper solution resulting in a bilayer structure, (c) removal of the template, and (d) release of the nanowires facilitated by ultrasonic agitation.
Figure 17. Fe-Ni-Co nanowire with Cu-Fe-Ni-Co thinned segment was fabricated according to the same conditions as mentioned in section 3.4. The released Fe-Ni-Co nanowires were dipping in Au solution for certain time for electroless deposition..................................................48

Figure 18. Flow-chart of the KMC simulation used in this project.........................53

Figure 19. Fe-Ni-Co RCE thin film galvanostatic deposition (a,b,c) at a constant rotation rate, 1000 rpm, and (d,e,f) at a constant applied current density –50 mA/cm²; (a,d) composition (b,e) corresponding current efficiency and (c,f) partial current densities.........................................................61

Figure 20. RCE polarization curves on Fe-Ni-Co thin films fabricated at -50 mA/cm² in a Fe-Ni-Co electrolyte polarized in the (a) cathodic direction at different rpms, (b) anodic direction at different pHs, rotation rate: 1000 rpm...........63

Figure 21. Potential and current transients during nanowire fabrication, (a) Fe-Ni-Co pulse cathodic current deposition (step 1), (b) anodization by different applied anodic potentials (step 2), and (c) Fe-Ni-Co pulse cathodic current following the previous anodization treatment (step 3)..................................67

Figure 22. TEM images of nanowires fabricated with the intermediate, second layer deposited at an applied potential of 0.4 V vs OCP before etching; (a) low and (b) higher magnification. SAED results for the (c) oxide region that was reduced and (d) Fe-Ni-Co region...............................................................68

Figure 23. Nanotips fabricated by etching nanowires in a pH 5 citrate-boric solution. Evolution of nanotips structure (a-f) with an increase in overpotential (0 V vs OCP – 0.6 V s OCP)...............................................................70

Figure 24. Nanotips structure fabricated with the anodic potential of 0.2 V vs OCP and etched without agitation (a) low magnitude image, (b) high magnitude image............................................................70

Figure 25. Schematic illustrating the progression of the electrochemically fabricated multilayered nanowires with embedded porous regions as a precursor for nanotips with corresponding potential transients. (a) pulse deposition of the first layer of Fe-Ni-Co, (b) an oxide layer was generated through an applied cathodic potential, (c) an immediate pulsing deposition was applied after the oxide layer to reduce the oxide and deposit Fe-Ni-Co simultaneous, (e) growth of the second layer Fe-Ni-Co...............................77
Figure 26. The rotating cylinder working electrode (a) apparatus and (b) resulting polarization curves of a Fe-Ni-Co deposit fabricated at –50 mA/cm² being anodized in a citrate acid electrolyte at different pH, scan rate = 2 mV/s.

Figure 27. Polarization curves of a Cu being anodized in a citrate-boric acid electrolyte at different pH, scan rate = 2 mV/s.

Figure 28. Fe-Ni-Co nanogaps fabricated with electrodeposited Cu as the sacrificial layer, copper layer was electrodeposited at –3 mA/cm² for (a) 50 sec, (b) 10 sec, and (c) 0.02 sec. The Fe-Ni-Co/Cu/Fe-Ni-Co tri-layered nanowires were etched electrochemically at 0.4 V vs OCP for 1 min.

Figure 29. (b-e) SEM image of tri-layered Fe-Ni-Co/Cu-Fe-Ni-Co/Fe-Ni-Co nanowires after exposure to the copper-citrate electrolyte with the copper ion concentration 0.15 M, 2 min, at variable pH: 0, 1, 2 and 4. (f) A summary of the penetration length with the proton concentration. Scale bar 1000 nm.

Figure 30. Nanowire tri-segment thinning procedure pH effect on the penetration length. (a) procedure as in Figure 15, with an additional layer of Fe-Ni-Co following the acid copper ion solution treatment. (b-e) SEM image of tri-layered Fe-Ni-Co/Cu-Fe-Ni-Co/Fe-Ni-Co nanowires after exposure to the copper-citrate electrolyte with the copper ion concentration 0.15 M, 2 min, at variable pH: 0, 1, 2 and 4. (f) A summary of the penetration length with the proton concentration. Scale bar 1000 nm.

Figure 31. SEM-EDS mapping for tri-layered Fe-Ni-Co nanowires with intermediate Fe-Ni-Co-Cu thinning segments before etching. (a) Sketch and SEM images for nanowires before etching, Fe-Ni-Co was immersed in Cu(II), pH 1 solution for 2 min. (b-e) EDS analysis for element of Fe, Ni, Co and Cu respectively.

Figure 32. Cu-citrate complex species distribution as a function of solution pH.

Figure 33. Fe-Ni-Co nanowires before and after etching. (a) Sketch before etching, (b-c) TEM and SEM images. (d) EDS analysis. (e) Sketch after etching in a pH 0 boric acid-citrate electrolyte, 30 s. (f-h) TEM and SEM images. (h) EDS analysis.

Figure 34. Copper concentration effect on penetration length. SEM images of Ni-Fe-Co nanowires after dipping into the copper-citrate electrolyte with
varied copper ion concentration of (a) 1/10X, (b) 1/5X, (c) 1/2X, (d) 1X and (e) 2X, X=0.15 M, pH=1, dipping time and etching time 2 min. (f) The summary of the penetration length with copper concentration. Scale bar 1000 nm.

Figure 35. \([H^+]/[Cu(II)]\) effect on penetration length. SEM images of Ni-Fe-Co nanowires after dipping into the copper-citrate electrolyte with varied proton and copper ion concentration, with a ratio of (a) 0.2, (b) 0.4, (c) 0.8, (d) 1.6, and (e) 3.2, total reactants concentration 0.4 M, dipping time and etching time 2 min. (f) The summary of the penetration length with \([H^+]/[Cu(II)]\). Scale bar 1000 nm.

Figure 36. Varying dipping time induce penetration rate change, the concentration of \(Cu^{2+}\) effect the ion penetration from kinetic control to mass transport control, pH 1.

Figure 37. Scaled penetration rate. Experimental data, circles, compared to a simple fitted kinetic model, curve that describes the anodization of Fe by copper ion reduction and proton reduction, dipping time and etching time 2 min.

Figure 38. Etching time effect on penetration length. (a) TEM image of nanowires after dipping them into a copper-citrate electrolyte, pH 1, copper ion concentration 0.15 M, 2 min. (b-d) TEM images of nanowires after dipping them into a copper-citrate electrolyte, and subsequently etching them in a pH 5 boric acid-citrate electrolyte for 1, 3 and 5 min.

Figure 39. KMC simulation of Cu(II) propagation into a Fe-Ni nanowire. (a) Fe(71%)-Ni(29) alloy before Cu(II) penetration, (b) Cu-Fe-Ni porous nanowires after Cu(II) penetration and dealloying. Simulation size 20X20X100, total KMC simulation steps = 20000.

Figure 40. KMC simulation of pure, solid copper nanowire thinning, from left to right are initial copper nanowire, copper nanowire after thinned by 400 KMC steps, 800 KMC steps, 1200 KMC steps, and 1600 KMC steps, respectively.

Figure 41. KMC simulation of porous copper nanowire thinning. Initial Cu-Fe-Ni nanowires containing 8.9% of Fe and Ni atoms (a), 16.9% of Fe and Ni atoms (b), 19.8% of Fe and Ni atoms (c), and 31.6% of Fe and Ni atoms
(d), are thinned and tracked. For each group of simulation, from left to right are initial copper nanowire containing, copper nanowire after thinned by 400 KMC steps, 1200 KMC steps, 2000 KMC steps, respectively. The image in box is a local room in result to show more detail. .................................109

Figure 42. (a) Low magnification SEM of a collection of Fe-Ni-Mo nanowires with an average composition of 57 wt % Fe, 18 wt % Ni and 26 wt % Mo, (b) Deposit composition after the array of Fe-Ni-Co nanowires were dipped into the pH 1, copper-citrate solution, (c) SEM image and select area EDS composition analysis for a collection of bi-layered Cu-Mo-iron group/Fe-Ni-Mo nanowires formed in a pH 1, copper-citrate solution for 120 s, (d) EDS mapping analysis for Cu.................................................................113

Figure 43. HRTEM (a) low resolution images of bi-layered nanowires fabricated by dipping Fe-Ni-Mo nanowires in pH 1 copper solution for 120 s, (b) high resolution image of the middle region of the nanowire and the corresponding (c) SAED of the middle region; (d) high resolution image of the tip region and the corresponding (e) SAED for the tip. Scale bar for (b) and (d) are 100 nm [152]. .................................................................................115

Figure 44. (a) HRTEM images of the Fe-Ni-Co nanowires with the thinned region after dipping in gold solution for 10 min. (b) the SAED pattern of the thinned region. The white label represents Ni, the yellow labels represents gold. ..........................................................................................................................117

Figure 45. SEM image of Fe-Ni-Co nanowires with thinned region after coated with gold (a), and EDS-mapping of elements, (b) Au, (c) Cu, (d) Fe, (e) Ni, and (f) Co. ......................................................................................................................................117

Figure 46. Comparison of Fe-Ni-Co nanowires alignment via magnetic thin film combined without extra magnetic field (a) and with extra magnetic field (b). ..................................................................................................................................119

Figure 47. (a) schematic of proposed nano-sensor platform for biomolecular detection, (b) Fe-Ni-Co nanowires aligned on top of nanofluidic channels..........119
LIST OF TABLES

Table 1. Standard electrode potentials in aqueous solutions at 25 °C in V vs SHE (standard hydrogen electrode) [68]...................................................................................................27
Table 2. Composition of Fe-Ni-Co, and etching electrolyte.............................................38
Table 3. Electrolyte composition of a (a) Fe-Ni-Mo deposition solution, (b) Cu dipping solution........................................................................................................................................44
Table 4. Bonding energies for different metal atoms and electrolyte...............................55
Table 5. Equilibria reactions and corresponding stability constants from citrate solution. (A represents C₆O₆H₄)........................................................................................................91
1 INTRODUCTION

Nanotechnology, since its boom from 2001 [1], has enabled the design of new materials, and sensing devices. In 1676, Van Leeuwenhoek first discovered red blood cells and microorganisms by using an improved optical microscope [2], and the discovery of the micro world extraordinarily promoted modern medicine. Today, nanotechnology holds the potential to do the same for modern medicine, to help understand things which are more fundamental components of the biological world, e.g. bacteria (0.3µm – 5µm), virus (20 nm – 400 nm) and DNA (~2 nm).

The progress of nanotechnology in the past several decades made it possible for people to observe and inspect matter at the nanoscale. Take the Human Genome Project, which for the first time identified and mapped all of the genes of the human genome in 2003 as a landmark; since then, DNA sequencing technology has experienced three generations: Sanger’s chain-termination method [3, 4] as the first generation, PCR amplification as the second generation [5], and single-DNA sequencing as the third-generation, (for a comprehensive review of those three generation DNA sequencing technology, see [6]). Consequently, the cost per genome
decrease from $100M (2001) to $5K (2013)[7] and the current hope is to achieve sequencing at a cost below $1K [8].

The urgent hurdle for DNA sequencing engineers is how to lower the price of personalized gene sequencing and to do it rapidly, to aid clinicians at the bedside. A general idea is sensing a single molecule sequence read out directly, without any amplification, or fluorescent labeling, through the distinct transverse electrical conductivity of each DNA nucleotide passing through a pair of electrodes. In the request of the $1,000 genome project sponsored by National Human Genome Research Institute, Soper et al. [9] developed a new single-molecule detection method by means of “time of flight analyses” that required a pair of nanoelectrodes place in a nanofluidic channel. The principle of this method is based on the mobility of nucleotides. As a part of this larger project, our aim is to examine the limits of fabricating a nanowire with a well-controlled nano-gap and create multiscale electrodes that is to be used for this project. The following criteria are to be met: 1) the technique is to be cost effective and not use high-end tools, such as e-beam lithography, 2) the nanowire will have the ability to be moved into position in a
micro-device, 3) is corrosion resistant, and 4) the gap will be controlled between 1-10 nm with a resolution of 1 nm.

Current methods for fabricating sub-10 nm nanogaps typically rely on: mechanically controllable break junctions, first reported by Read et al. [10] in 1997 by using notched gold wires, generated a nanogap with a size ~1 nm, the electromigration method using an electron wind force to break a nanowire, which can finally form a gold nanogap with a size of 1 nm [11], focused ion beam [12], electron beam lithography[13] (for a comprehensive understanding, see review [14]). Sub-10 nm nanogaps, even <1 nm nanogap have been made through those methods. However, they are far from practical considering the instruments used during the fabrication process. It’s also worth noting that most of the metallic materials used for the aforementioned nanogaps were either expensive gold or platinum. Here, two approaches taken are to create nanowires by electrodeposition into a porous template with Super Invar (64 wt % Fe, 31 wt % Ni, and 5 wt % Co) as the main structural component. In the first approach, the nanogaps are obtained through chemically etching a deliberately fabricated intermediate layer with gradient porosity and
crystallinity. In the second strategy, a modulated thinning nanowire segment in between two larger nanowire segments was fabricated via a coupled displacement/dealloying and followed by an etching reaction. Nanogaps were envisioned to be placed into a nanochannel. A gold layer is then coated over the nanowires, in the form of a core-shell design, to complete a corrosion resistant design and to provide enhanced electrical conductivity.

Template electrodeposition has been chosen as the method to fabricate nanowires because of its ease to be scalable, economic fabrication cost, and is widely researched. Porous anodic alumina and polycarbonate are two most commonly used templates for nanowire deposition, and both are commercially available. In our research, polycarbonate was chosen as the template. Super Invar has been chosen as the main region of the nanowire; it is of interest, because of its high magnetic moment in order to magnetically position the nanowires, unique low thermal expansion property that can be tailored by the composition, and corrosion resistance once passivated. Alloys of Fe-Ni-Co exhibit quite different corrosion resistance at different percentage of Fe and Ni, which can be advantageously used to fabricate a nanogap
through selective etching.

To survey deposit and etch conditions of Fe-Ni-Co, Fe-Ni-Co oxide, and Cu in different solutions, polarization curves were examined by using a rotating cylinder electrode (RCE) set-up. Alloy composition was analyzed with XRF, and FESEM-EDS, and surface morphology, crystallinity, and porous structure were monitored with FESEM-EDS, TEM and HRTEM. A Kinetic Monte Carlo simulation was also developed to simulate the metal ion reaction rate that propagates into the nanowire for the fabrication of a new methodology to create multi-sized nanowire segments.
2 LITERATURE REVIEW

2.1 DNA sequencing

Heritage information, cancer evolution, family history and almost all other kinds of genetic information are coded in our DNA, which is composed of four basic types of nucleotides. A nucleotide consists of a molecule of sugar, a phosphoric acid group and one of four possible nitrogen containing bases: adenine (A), thymine (T), guanine (G), and cytosine (C) [15]. DNA sequencing can advance the understanding, treatment, and prevention of human and plant diseases; to appreciate the complexity of the problem it is interesting to note that it took the Human Genome Project 13 years and $3 billion to get the sequence of three billion bases of the human genome in 2003 [16]. Three generations of DNA sequencing methods were developed after that with the goal to lower down the price of DNA sequencing to $1,000, to make it routine, fast and affordable [17].

Sample preparation, physical sequencing, and re-assembly of the DNA strand are the three steps for typical DNA sequencing [18]. Specifically, sample preparation requires breaking the target gene into segments with different lengths, an
amplification step can make tens of thousands copy of those segments. Physical sequencing is used to read out the genome sequence for each segment. Finally, bioinformatics software is utilized to repositioning of these segments and excluding the overlapping part [17].

2.1.1 First-generation of DNA sequencing

The first-generation DNA sequencing technique (chain-termination method) was developed by Sanger-[3, 4] who was awarded the 1980 chemistry Noble Prize “for his contribution concerning the determination of the base sequences in nucleic acid” [19]. Sanger’s DNA sequencing method was easy to operate and scale up, and quickly became the dominant way for DNA sequencing at that time.

Figure 1 shows traditional chain-termination method for DNA sequencing compositied of a single-stranded DNA template, a primer DNA polymerase, normal deoxycleotidetriphosphates (dNTPs), and modified di-deoxynucleotidetriphosphates (ddNTPs) [20]. In Figure 1(a) the primer, which is a short strand of nucleic acid sequences, was used to start the chain reaction. In Figure 1 (b), DNA samples were separated into four groups. Each group containing all four of the standard
deoxynucleotides (dATP, dTTP, dCTP, and dGTP) and one type of
di-deoxynucleotidetriphosphates (ddNTPs). dNTPs were the composition of DNA
strands used here for elongation of primer; ddNTPs have similar structure of dNTPs
but lack a –OH group, which can be used to cease extension of DNA. Through
adjusting the proportion of dNTPs and ddNTPs, fragments with different lengths will
be prepared. The resulting DNA segments were separated by size using gel
electrophoresis (Figure 1 c). The sequencing of template DNA can be read out
through this method. In the original publication in 1977 [4], sequences from 15 to 200
nucleotides from the priming site can be determined with reasonable accuracy using a
single primer.

Hood and coworkers [21, 22] improve this method in 1986 with fluorescently
labeled ddNTPs and di-primers, for high-throughput DNA sequencing. However,
software that translates these fluorescent signals into a DNA sequence will inevitably
generate error probabilities [23, 24]. Simultaneous electrophoresis in 96 or 384
independent capillaries provides a limited level of parallelization, which actually
made it not helpful for wide-ranging applications.
2.1.2 Second-generation of DNA sequencing

To overcome the low-throughput and high cost problem of the first-generation sequencing, second-generation sequencing was germinated around 2005. Illumina’s HiSeq and Roche’s 454 are two typical second-generation sequencing techniques, both methods read DNA sequences during nucleic synthesis. Two things were introduced: large-scale identical detectors and improved polymerase chain reaction amplification (PCR). A large-scale identical detector promises tens of thousands of
physical sequencing steps that can proceed simultaneously (Figure 2), leading to extremely high throughout and a resultant low cost. Illumina’s HiSeq 2000 instrument can process 200 gene expression samples in a single run for under $10,000 per sample [26]. PCR was developed in 1983 by Kary Mullis [27, 28] for amplifying a single DNA to thousands of copies. In the second-generation DNA sequencing, improved PCR amplification methods such as emulsion PCR or bridge PCR were applied to obtain a large number of DNA segments without the conventional bacteria-based amplification stages used in Sanger’s sequencing, which make large-scale sequencing possible.
Figure 2. Illumina workflow. Starting from fragmentation and adapter ligation steps, after adhesion to a solid surface, an isothermal process is used for DNA segment amplification into a cluster. The cluster fragments are annealed with a sequencing primer and subjected to sequencing by synthesis using labeled nucleotides. A sequence is finally read out through imaging [29]. (see [30] for more details)

The disadvantage of second-generation sequencing is the inevitable amplification bias in the PCR amplification step and the subsequent noise seriously affects the measurement accuracy. Another problem is that second-generation sequencing still relies on color discrimination of fluorescently labeled nucleotides,
which make it hard to go to extremely low cost. Therefore, a new generation of DNA sequencing methods that aims to read DNA sequences directly based on the physical property of nucleotides, without any amplification and fluorescent labeling is most desirable.

2.1.3 Third-generation of DNA sequencing

Third-generation sequencing tries to read single nucleotides directly, without amplification or fluorescent labeling. Sensing is done through monitoring transient changes in ionic current through a nanopore, transverse electrical currents [31], and transverse differential conductance [32], which depends on the differences in the electronic capacity of the DNA nucleobases. To this end, graphene nanopores have been used [33, 34], based on the ultra sensitivity of graphene to subtle variations in local electric potential fields. Sequence-specific hysteresis was exhibited in an alternating electric field [35], in a single nanogap and nanofluidic channel [36], and in a “time of flight” method [37], which distinguish nucleotides through the motion of a single nucleotide in a nanofluidic channel.

Single-molecular detection must overcome the problem of efficiently and
accurately obtaining distinct signals from individual nucleobases separated by sub-nanometer dimensions, as well as developing reproducible pore sizes of similar size in an economic way. Therefore, detectors at the nanoscale are one of the key hurdles for third-generation sequencing from laboratory to factory. Instruments that are used for third-generation sequencing include: nanopores (α-hemolysin) [38], MspA protein [39], graphene [40, 41]) nanofluidic channels [42] and nanogaps [36].

In Chapter 2.2, the progress of nanogap fabrication is discussed.

2.2 Nanogap fabrication

Nanogaps for small molecular detection, such as DNA, require gaps to be < 10 nm at least in one dimension, because the target molecules are at the same order. Typically, there are two methods to build nanogaps: bottom-up and top-down.

2.2.1 Mechanical break junctions

Mechanically controllable break junctions were first reported by Tour and coworkers in 1997 [10, 43]. Figure 3 illustrates the principle of this method. First, a notched Au nanowire is fixed on the substrate. An atomically sharp nanogap can be generated after bending the substrate. The distance can be controlled by a
piezoelectric element. The authors also designed a mechanism to bring the nanogap back into contact, utilizing a solution of 1 mM benzene-1,4-dithiol in a THF solvent, self-assembled monolayer can form on the facing Au electrodes generated by the mechanical break. Through detecting the onset of conductance, researchers can figure out when the self-assembled monolayer was sealed. While generating a nanogap by controlling a piezoelectric element was easy to do, the resulting gap has limited size control and can be only several molecules big. Additionally, the method was limited to certain materials (i.e., Au) which can support the self-assembly.

![Mechanical break junction method for nanogap fabrication](image)

Figure 3. Mechanical break junction method for nanogap fabrication [44].

2.2.2 Gap narrowing by electrodeposition or chemical deposition

Electrodepositing metal atoms onto large facing electrodes can narrow the gap size from the original hundreds of nanometers (nm) to the domain of a few nm, which
is another way to make nanogaps [45]. Recently, researchers advanced this method by combining an impedance feedback system (Figure 4). The electrochemical deposition process stops when the feedback system signal reaches a preset value, inducing a controllable gap width between 20 to 3 nm [45, 46]. Liu et al. [47] improved this method by using a high-frequency impedance system as feedback to detect the changes on voltage-time curves. When the two electrodes, in this case, the two nanoscale facing tips, were closed enough, the electrical double layer will generate a tunneling region, where current is extremely sensitive to distance. By monitoring the shift change of this tunneling current, the deposition can be terminated with the aid of a computer program, and the nanogap with finely controlled sizes are obtained. Their results show nanogaps ranging from 1 nm to >10 nm reproducibly obtained by detecting the phase-shift changes.

The most important feature of the feedback electrodeposition method for nanogap fabrication is its high sensitivity and computer assisted operation, which brings extreme accuracy of gap size control. However, electrodeposition and the feedback system is hard to make sharp tips, and also considering that the seed tips
usually come from the use of electronic ion lithography, or the focused ion beam method, the resulting methodology is an obstacle for large-scale application. Another disadvantage is that the tips fabricated by electrodeposition generally have a rough surface because of the mass transport control of electrodeposition.

![Electrodeposition and feedback system for nanogap tuning](image)

\[Figure 4. Electrodeposition and feedback system for nanogap tuning, (a) two sharp tips with a distance ranging from 200 nm to 500 nm fabricated by focused ion beam. (b) < 10 nm nanogap formed by electrodepositing metals outside of the tip; a feedback system was used to control the final gap size [45].

2.2.3 Electromigration

Electromigration is the transport of material caused by the gradual movement of ions in a conductor due to the momentum transfer between conducting electrons.
and diffusing metal atoms [48]. Electromigration decreases the reliability of integrated circuits by breakdown of the wires at high currents. However, this property can be utilized for fabricating nanogaps. By finely controlling the gate voltage, a 1 nm nanogap can be obtained from a 100 nm wire prepared by electromigration [11].

Electromigration induces a break-junction phenomenon related to several factors such as diffusion, thermal effects, substrate materials, and temperature, therefore, by refining the electromigration procedure and conditions, researchers have achieved reproducible, finely controlled Au nanogaps [49]. There are two major issues for using the electromigration break-junction method for nanogap fabrication. First, high-end tools are needed to fabricate the nanostructure (the nanowire in Figure 5). Secondly, the size and shape of as-prepared nanogaps by electromigration was not easy and sometimes difficult to control [50].
2.2.4 Focused ion beam

Focused ion beam, (FIB), uses ions (usually gallium) for imaging, sputtering, or milling samples based on the current, temperature, and focused resolution that is used. An ordinary FIB has a resolution of 5 nm, which make it a good candidate for nanostructure fabrication.

Hu and collaborators [51] use FIB milling (Figure 6) successfully to achieve reproducible nanogaps with gap-width down to 1-2 nm. In their method, suspended Au nanowires were attacked by the focused ion beams to form a grain boundary. The grain boundary was subsequently “grow up” by FIB milling. The authors think the enlargement of the gap-size was due to a temperature rise at the milling site which

Figure 5. Schematic of an electromigration break-junction induced nanogap [49].
accelerates the departing atoms. Another critical factor is that FIB irradiation will tend to bend the tips in the direction of the beam.

Figure 6. Illustration of focused ion beam milling substrate [52].

Generally, during the FIB manufacturing process, the top layer of atoms will be etched for a long time compared to the bottom layer of atoms. Melting and burning may happen at the top layer of atoms to create a FIB tail at the end. Nagase [53] developed a FIB sputter etching method with in situ monitoring of etching by measuring the current through the patterned electrode films. Using this method, a uniform 3 nm nanogap was successfully prepared on a 50 nm wide Ti/Au/Ti nanowire. Because of the tri-layer structure design, the FIB tail was successfully avoided.
However, FIB can only be used on nanostructures as a seed substrate, which needs to be fabricated by electron beam lithography, or photolithography, which sets an obstacle for mass production and repeatability.

### 2.2.5 Silicon tip sharpening

A silicon tip sharpening technique was first suggested by Marcus and his collaborators [54-56] in the 90s for preparing AFM tips. Han et al. [57, 58] improved this method for nanogap fabrication, as shown in Figure 7, using conventional optical lithography, and low-pressure chemical vapor deposition to prepare the silicon substrate. A KOH anisotropic etching was subsequently applied for the fabrication of the silicon nanogap. The smallest radius was formed when the top silicon layer was exactly etched, therefore, the etching rate and the etching time was the key factors for this method. Theoretically, this method can be applied to other metals for preparing nanogaps.
Figure 7. Schematic illustration of silicon etching for tip sharp, (a) a tip with 200 nm - 300 nm top layer before etching, (b) a nanogap prepared after etching the top layer [58].

2.2.6 Molecular ruler

Motivated by the nano size of molecules, researchers developed a method by using molecules as templates to prepare nanogaps [9, 59]. In Hatzor’s work, [59] highly polished 40 - 100 nm wide Au parallel traces were fabricated through electron-beam lithography (Figure 8 a). Mercaptoalkanoic acid was coated on the Au surface through layer-by-layer assemble, which fundamentally relies on metal-organic coordinates. Consequently, the thickness of the mercaptoalkanoic acid layer can be controlled by how many layers were assembled on the Au surface (Figure 8 b). The
third step is coating metal from the top to seal the whole setup. From another aspect, the gap size depends on how much organic molecules were removed between Au and deposited metal (Figure 8 c, d). By using this method, ~15 nm nanogaps can be obtained. A similar method was applied with cross EBL lines to create nanogaps [60].

The molecular ruler method masterly utilizes the layer-by-layer assemble ability of organic molecules to control the gap size. This method is easy to mass produce, and can be precisely controlled. But the introduction of EBL to prepare the parent materials unfortunately lowers the manufacturing efficiency.
Figure 8. Schematic of the scaling-down process. (a) Electron-beam lithography forms the parent structures (yellow rectangles), (b) layer-by-layer construction of metal-organic resist (2 nm per layer). The arrow represents the mercaptoalkanoic acid (tail is the SH group). (c) Metal (Blue arcs and rectangle) evaporation into the gap (the gap size is determined by the number of organic layers deposited), and (d) Lift-off of the organic layer in HCl/DMF solution [59].

2.2.7 Template electrodeposition

Template electrodeposition is a high throughput method to fabricate nanostructures, particularly nanowires, as an alternative of lithography. Arrays of
nanowires are obtained by filling a porous template that contains a large number of pores with diameters adjustable from 10 to 2,000 nm. Commonly used templates are anodized aluminum films and polycarbonate films, which are commercially available. A typical procedure of using template electrodeposition to fabricate nanogaps is shown in Figure 9. A thin layer of gold is sputtered on one side of the membrane acting as the working electrode (Figure 9 a); another function of this thin layer of gold is to seal the nanopores, preventing electrolyte from draining out. Then metal is then electrodeposited into the pore, followed by a second metal, and then a third layer. The materials can be metal or conductive polymers [61]. Subsequently, the polycarbonate membrane was dissolved by dichloromethane (Figure 9 e) to liberate nanowires followed by dispersing them with ultrasonication (Figure 9 f). Finally, the middle-layer metal can be selectively removed by chemical or electrochemical methods to create a gap in the middle (Figure 9 g). By using this method, Au-Ni-Au,[62] Au-Ag-Au,[62, 63] Pt-Ni-Au,[64] Fe-Ni-Co/Cu/Fe-Ni-Co[65] nanogaps have been successful prepared. Mirkin et al.[66] advanced this method to on-wire lithography, by deposited multi-segments nanowires with sophisticated
controlled lengths of the sacrificial layer, and showed varying gaps that were obtained on a single nanowire.

Dasilva *et al.* [67] found that electrodeposition doesn’t work well to fabricate ultra small gaps, *e.g.* <3 nm, when using silver as the sacrificial layer. He stated that the reason is due to the fast growth rate (low overpotential) of Ag\(^{2+}\) reduction that makes electrodeposition extraordinarily challenging to obtain a very thin (<3 nm) layers of Ag. Therefore, electroless deposition was selected as an alternative method for Ag layer fabrication. Sub-3 nm Au-Ag-Au nanogaps were successfully prepared through this method [63].

Figure 9. Schematic of nanowire fabrication using a nanoporous membrane as a template. (a, b, c, and d) multi-segments of nanowires deposited (e and
f) liberated nanowires. (g) chemically or electrochemically etching the sacrificial layer to obtain gaps on nanowires.

2.3 Electrodeposition and three electrodes system

Electrodeposition is an economical technique that has been used for more than a century to fabricate films, its utility in nanowire fabrication, however, was started by the seminal work by Martin [68] during the early 90s. using alumina nanoporous templates. Subsequently, track-etched polycarbonate membrane was also created for nanowire preparation. Now, both of them are commercially available.

A typical electrochemical cell is composed of three electrodes. In the case of electrodeposition, the cathode is the working electrode, where the reduction reaction happens. Basically, a metal will be deposited to form a solid when the applied potential of the working electrode is more negative than it’s equilibrium potential. Standard electrode equilibrium potentials of related materials in aqueous solutions are listed in Table 1. The counter electrode is typically made of materials with a high equilibrium potential (e.g. Pt, C), which keeps them from dissolving during the electrochemical reactions. Reference electrodes have a stable interfacial potential when the electrochemical reactions occur on the cathode and anode. They are used to
monitor the working electrode potential change, which is extremely helpful for electrodeposition. As an example, three of the most commonly used reference electrodes are the standard hydrogen electrode (SHE, 0 V), saturated calomel electrode (SCE, 0.241 V vs SHE), a silver/silver chloride (Ag/AgCl, 0.198 V vs SHE).

Table 1. Standard electrode potentials in aqueous solutions at 25 °C in V vs SHE (standard hydrogen electrode) [68].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Potential</th>
</tr>
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<tbody>
<tr>
<td>Au⁺ + e ⇌ Au</td>
<td>1.83</td>
</tr>
<tr>
<td>Co²⁺ + 2e ⇌ Co</td>
<td>-0.277</td>
</tr>
<tr>
<td>Cu²⁺ + 2e ⇌ Cu</td>
<td>0.34</td>
</tr>
<tr>
<td>Fe²⁺ + 2e ⇌ Fe</td>
<td>-0.44</td>
</tr>
<tr>
<td>2H⁺ + 2e ⇌ H₂</td>
<td>0.000</td>
</tr>
<tr>
<td>2H₂O + 2e ⇌ H₂ + 2OH⁻</td>
<td>-0.828</td>
</tr>
<tr>
<td>O₂ + 4H⁺ + 4e ⇌ 2H₂O</td>
<td>1.229</td>
</tr>
<tr>
<td>O₂ + 2H₂O + 4e ⇌ 4OH⁻</td>
<td>0.401</td>
</tr>
<tr>
<td>Ni²⁺ + 2e ⇌ Ni</td>
<td>-0.257</td>
</tr>
</tbody>
</table>

2.4 Sculpting nano-features with displacement and dealloying reactions

Displacement reactions involving a more noble elemental ion that is reduced at the expense of anodizing a less noble material can cover the surface of the less noble material in a self-limiting way. Recently, displacement accompanied by interstitial solid state diffusion, has been shown to form unique structures at the
The initial displacement reaction can generate a thin layer of a noble material at the surface of a less noble substrate, however, surface pinholes allow the reaction to continue into the less noble solid structure resulting in hollow or porous nano-architectures. The displacement of silver by the reduction of AuCl$^{4-}$ and subsequent diffusion of gold onto and into silver spheres and cubes resulted in hollow nanostructures [71-73] and porous wires [73, 74]. Similarly Bi$^{3+}$, and HTeO$^{2+}$ reduction on nickel nanowires [75] resulted in high-aspect ratio nanotubes. The valence of the more noble material, as well as the stoichiometric relationship between reactants (e.g., contrast $PtCl_6^{2-} + Te$ versus $2Pd^{2+} + Te$) is an important factor on the as-obtained structures being either hollow or solid (see Figure 10) [76]. Suh et al.[77] fabricated tapered and dumbbell shaped nanowires by creating electrodeposited multilayered nanowires having disparate Ni-Fe composition followed by a displacement reaction once the nanowires were removed from the template, with the more noble bismuth and tellurium ions. The displacement reaction favored the less noble Fe-rich segment and resulted in thicker segments. From the same group, interesting tellurium nanotubes containing gold particles were fabricated.
by the displacement of a template-assisted electrodeposition of Co/Au layered nanowires with the cobalt layer sacrificially displaced by tellurium in a non-uniform way [78].

![Diagram of Pd nanotube and Pt nanowires fabrication using displacement reaction with Pt nanowires][76]

**Figure 10. Schematic illustration of Pd nanotube and Pt nanowires fabrication using displacement reaction with Pt nanowires [76].**

Dealloying has been well known to occur in a metal alloy and undergoes selective dissolution creating a spongy surface and internal island structure [79, 80], and there has been renewed interest in this effect for the generation of nano-scale porous architectures that can be generated through this technique (Figure 11). Laocharoensuk *et al.* [81] created interesting tapered, step-cone nanowire segments of gold by electrodepositing a series of gold-silver alloy layers sequentially with different composition and then by dealloying them, removing the silver. Similarly,
nanowires created with a template having a modulation of porous gold segments, between a solid gold segment, created nano barbells generated by switching between two different plating electrolytes, one for gold and another for the silver-gold alloy. The silver was dealloyed to create the porous region. Dealloying of one component in an unmodulated electrodeposited alloy nanowire was presented by Liu et al. [82]. They electrodeposited a Co-rich, CoPt alloy into an aluminum oxide membrane, and then partly removed cobalt by chemically etching it to create porous nanowires having ultra-small pore sizes between 1-5 nm.

Figure 11. Schematic illustration of porous structure generated by dealloying reaction.

2.5 Nanotip fabrication

Nanowires that are shaped into tips at one end, nanotips, have been widely researched due to their application as cantilever tips for high-resolution atomic force microscopy (AFM) [83, 84], tip-enhanced near-field optical microscopy [85], and
scanning tunneling microscopy (STM) [86-88], and the need has recently expanded to bio/chemical sensors to measure electrical conduction as a new methodology for molecular detection and monitoring [65, 89-91]. The reported nanotip materials used in AFM/STM are usually W and Pt/Ir, which are prepared through a “drop off” technique, where the tungsten wire is immersed in a KOH solution (etchant) acting as an anodic electrode; the highest etching rate appears just below the air/electrolyte interface, causing necking and eventual “drop off” of the bottom part of the wire, leaving a sharp tip [83, 86, 88, 92, 93]. Alternative methods for fabricating nanotips include: focused ion beam (FIB) lithography [53], vapor-liquid-solid method (VLS) [94, 95], and a novel, self-masking technique where SiC nanosized clusters are generated on top of a substrate, followed by a dry etch of the unmasked substrate regions to create nanotips where the SiC clusters reside [96].

2.6 Cu-Mo nanowires

Cu-Mo alloys combine the high thermal conductivity of Cu with low thermal expansion of Mo [97, 98], owing to its low-miscibility [99], and finds use as materials for heat-sinks and spreaders in electronic devices [100-104]. To date, physical
methods (*e.g.* mechanical alloying [105], vapor deposition [106], rapid solidification [107]) and chemical methods (*e.g.* co-precipitation [108, 109], sol-gel [110]) have been utilized for Cu-Mo synthesis, however, few reports have been published for fabricating Cu-Mo films by electrodeposition [111, 112] and none as nanowires.

Currently, molybdate ions cannot be fully reduced in an aqueous electrolyte without a codepositing element, referred to as induced codeposition [111, 113, 114]. Typically, ions of the iron group elements, *e.g.*, Ni and Fe, induce best molybdate reduction to zero valence state Mo. The co-reduction of Cu(II) is recognized as also inducing the molybdate reduction reaction, but at a much lower extent. Recently, electrodeposited thin films of Cu-Mo with up to 22.9 wt % Mo, the highest amount of Mo induced by copper ions, has been achieved using citrate electrolytes [111, 112], although at relatively low current efficiency (20-40 %).

### 2.7 Monte Carlo (MC) and Kinetic Monte Carlo (KMC)

Monte Carlo (MC) simulation refers to a category of numerical analysis methods that is based on random numbers, just as the name connotes Monaco, a city famous for its gambling history. The modern version of the Monte Carlo method was
invented in the late 1940s by Stanislaw Ulam [115], while he was working on a nuclear weapons projects at the Los Alamos National Laboratory. The Monte Carlo approach is widely used in statistical physical, chemistry and materials research today, acting as an instrument in providing quantitative or semi-quantitative predication for of composition and structure, thermodynamic properties, phase diagrams, and free energies of systems; several review papers are available in this area [116-119]. In computational materials science, particularly, molecular dynamics (MD) simulation combined with Density Function Theory (DFT) allows one to follow the dynamics of molecular processes in great details. However, MC and KMC simulation expand the simulation time dramatically (from micro-seconds to min), when representing more practical applications [120].

One way to model molecular behavior with Monte Carlo is the Metropolis Monte Carlo, which was introduced to sample a Boltzmann distribution instead of accumulating configurations randomly, designed to automatically search the transition of configurations to a lower overall system energy and finally reach thermodynamic equilibrium. A typical algorithm for Metropolis Monte Carlo is as follows:
1) Generate a starting configuration $S_0$,

2) Select a new configuration $S_1$, which was generated randomly,

3) Calculate the energy change upon a configuration change $\Delta E$,

4) Calculate the probability for this configuration change to happen using a Boltzmann distribution:

$$ P = e^{-\frac{\Delta E}{kT}} \quad (1) $$

5) Generate a random number $J$, if $P < J$, execute the transition, otherwise, reject the transition,

6) Repeat step 2) until reach the set condition.

A Metropolis Monte Carlo algorithm is static and cannot be used to study the evolution of a system. A step forward from Metropolis Monte Carlo is Kinetic Monte Carlo, and first reported by Bortz, Kalos, and Lebowitz [121] applied to an Ising model of ferromagnetism with a so-called N-fold way for accelerating the process. The KMC model addresses the progression of a system and requires that all transients that can occur must be enumerated before the simulation, in contrast, MC however, sets no limit on the number of possible transitions, or they may even need to be
known to start the simulation. The KMC therefore has huge time savings on the computation due to the rejection free architectures and allows a prediction of changes with time [119]. The time increments are defined so that they relate to the local kinetics of the system.
3 EXPERIMENTAL

This section addresses the fabrication and characterization of Fe-Ni-Co nanotips, Fe-Ni-Co nanowires with thinned region, and Cu-Mo-iron group alloy nanowires.

3.1 Fe-Ni-Co nanotip

A rotation cylinder electrode (RCE) was used to characterize the deposition and etching behavior of Fe-Ni-Co alloy thin films. These conditions were then used to guide the fabrication of nanowires and nanotips. A summary of the electrodeposition and etching process of the nanowires is sketched in Figure 12 and the electrolyte composition listed in Table 2. The nanowires were electrodeposited through a template assisted electrodeposition method using polycarbonate membranes that had a thin layer of gold sputtered onto one side of the membrane (Figure 12a). The first layer of Fe-Ni-Co was pulse deposited (-50 mA/cm² for 2 s, 0 mA/cm² for 2 s) at 40 °C (Figure 12b). The potential was stepped to its open circuit potential (OCP) value, for 10 min or to an anodic potential, at different values vs OCP, for 10 s (Figure 12c), before the second layer of Fe-Ni-Co was deposited under the same condition (Figure
After deposition, the nanowires were released from the membrane by dissolving the membrane in dichloromethane under ultrasonic agitation (Figure 12e), following by etching in a pH 5 citrate-acid solution for 10 min (Figure 12f). A sketch of the applied current or potential waveforms is shown in Figure 12g. In step 1, the applied current is modulated with a square pulse for fabricating the first layer of the tri-layered nanowires; in step 2, an anodic DC potential, or its open circuit potential, is applied followed by another pulse cathodic current deposition in step 3. Note that the charge passed in the third layer is smaller than the first layer so that differences of length can be observed in order to identify which part of the nanowire is the top and bottom. Once the nanowires were released from the membrane, they were etched with electrolyte agitation.
Figure 12. Nanogap and nanotip fabrication schematic with different applied pulse current or DC potential waveforms. (a) Nanoporous template with a thin gold film layer, (b) first layer of Fe-Ni-Co was electrodeposited to partially fill the pores, (c) an anodic or OCP potential was applied to create an oxide layer, (d) a second layer of Fe-Ni-Co nanowire was electrodeposited on top of the oxide layer with the same condition as mentioned in step b, (e) the template was removed to release the nanowires, (f) nanowires were etched in a pH 5 boric-citrate solution for fabricating nanotips.

Table 2. Composition of Fe-Ni-Co, and etching electrolyte

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel (II) sulfamate</td>
<td>0.720</td>
</tr>
<tr>
<td>Iron (II) sulfate</td>
<td>0.155</td>
</tr>
<tr>
<td>Cobalt (II) sulfate</td>
<td>0.016</td>
</tr>
<tr>
<td>Boric acid</td>
<td>0.500</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>0.001</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>0.011</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>0.010</td>
</tr>
<tr>
<td>Sodium citrate</td>
<td>0.450</td>
</tr>
<tr>
<td>Boric acid</td>
<td>0.400</td>
</tr>
</tbody>
</table>

Potential and current transients were monitored using a Solartron SI 1287
potentiostat. For all the RCE polarization experiments, the scan rate was 2 mV/s. Thin films were deposited galvanostatically onto the RCE. The composition and current efficiency at different current densities and rotation rates were analyzed. The average deposit composition was characterized by XRF (Kevex, Omicron). The nanowires and their resulting gaps and tips were inspected by a cold field emission SEM (Hitachi S4800) (Figure 13a). High resolution TEM, (JEOL JEM-2010F) (Figure 13b) and selected-area electron diffraction (SAED) were used to examine the local structure near the interfacial region between nanowire layers.

![SEM (Hitachi -3800)](image1) ![HRTEM 2010F JEOL](image2)

**Figure 13.** SEM and HRTEM used in this project

### 3.2 Fe-Ni-Co nanogaps with electrodeposited Cu as sacrificial layer

Fe-Ni-Co and Cu passivation properties were examined at different pH values
using rotation cylinder electrode (RCE) experiments. The results were used to guide the etching process of the tri-layered Fe-Ni-Co/Cu/Fe-Ni-Co nanowires. Nanogaps in between Fe-Ni-Co nanowire segments were fabricated with Cu as the sacrificial layer following the similar procedure reported by Kim et al. [65] in our lab.

3.2.1 RCE experiments on Fe-Ni-Co and Cu

To survey conditions to etch either chemically or electrochemically in a citrate solution, polarization curves were examined. A rotating cylinder set-up was used so that the hydrodynamic environment near the electrode surface can be well maintained. Figure 1 shows the experimental set-up and a representative set of polarization curves on a large rotating cylinder electrode (d = 1 cm) covered with the Fe-Ni-Co deposited at -50 mA/cm² at 40 °C at a rotation rate of 1000 rpm. The resulting deposit composition was examined with x-ray fluorescence: 63 wt % Fe, 35 wt % Ni, and 2 wt % Co. The cylinders were electrochemically etched in a citrate-boric acid electrolyte (0.01 M sodium sulfate, 0.45 M sodium citrate, and 0.40 M boric acid). The resulting pH was 7.5 and sulfuric acid was used to lower the pH to 5.

3.2.2 Fe-Ni-Co/Cu/Fe-Ni-Co nanowire fabrication and etching
The electrodeposition of nanowires was fabricated in a standard three electrodes cell with a nanoporous template. Figure 14 shows the schematic for Fe-Ni-Co nanogaps fabrication with electrodeposited Cu as the sacrificial layer. A polycarbonate membrane was first coated with a thin layer of Au by sputtering (Figure 14a), then the first layer of Fe-Ni-Co was pulse electrodeposited at -50 mA/cm\(^2\) (2 sec) and 0 mA/cm\(^2\) (2 sec) (Figure 14b), a short layer of Cu electrodeposited at -3 mA/cm\(^2\) for a certain time (Figure 14c), the second layer of Fe-Ni-Co was then electrodeposited at the same condition as the first layer of Fe-Ni-Co but a shorter time was used to distinguish which end is the top versus the bottom (Figure 14d), the nanowires were released from the membrane template (Figure 14e) and copper was electrochemically etched away at 0.4 V vs OCP for 1 min to create the gaps (Figure 14f). Guided by the RCE experiments, the deposit composition is expected to be rich in Fe at -50 mA/cm\(^2\) and rich in Ni at the lower current density -15 mA/cm\(^2\). A summary of the deposition condition is illustrated in Figure 14g. The Fe-Ni-Co nanowire was deposited from an electrolyte containing: 0.72 M nickel sulfamate, 0.155 M ferrous sulfate, 0.005 M cobalt sulfate, 0.5 M boric
acid, 0.001 M sodium lauryl sulfate, 0.011 M ascorbic acid, at a pH of 2 and temperature of 40 °C. After the first Fe-Ni-Co segment was deposited, the whole set up was immersed in a pH = 2 HCl solution to remove possible oxidation. Then a layer of Cu was deposited from an electrolyte containing: 0.15 M copper sulfate, 0.01 M sodium sulfate, 0.45 M sodium citrate, and 0.40 M boric acid.

Figure 14. Schematic for Fe-Ni-Co nanogaps fabrication with electrodeposited Cu as the sacrificial layer. (a) polycarbonate membrane was coated with a thin layer of Au by sputtering, (b) electrodeposited first layer of Fe-Ni-Co, (c) electrodeposited a short layer of Cu, (d) electrodeposited the second layer of Fe-Ni-Co, (e) release the nanowires from the membrane template, (f) electrochemically etching away Cu create the gaps.

3.3 Fe-Ni-Co nanowires with thinned segments

The procedure, the ensuing wire images, and deposit composition for corresponding steps to create the multi-scale wires are presented in Figure 15. Figure 15 is a schematic of the procedure: a nanoporous, polycarbonate membrane
(Whatman, porosity < 15%, diameter 50 nm) is rendered conductive by sputtering gold on one side of it (Hummer IV, 15 mA, 70 mTorr, 5 min); an Fe-Ni-Co nanowire segment is first pulse electrodeposited, partially filling up the depth of the template, with conditions provided by Kim et al. [65] Fe-Ni-Co wires were pulsed deposited at -50 mA/cm² for 2 s, and 0 mA/cm² for 2 s with the electrolyte shown in Table 3a, at 40 °C. The partially filled template is dipped into an acid solution containing copper ions to cause displacement, corrosion and dealloying of the Fe-Ni-Co alloy; the deposit is then removed and washed with DI water, and the template dissolved in dichloromethane; the released nanowires are then treated in a second solution that preferentially etches copper. The nanowires were inspected with field-emission scanning electron microscopy (FE-SEM, Hatachi - 3800) equipped with energy dispersive X-ray spectroscopy (EDS).
Figure 15. Nanowire bi-segment thinning procedure. (a) procedure: electrodeposition into a gold sputtered membrane, exposure of the membrane containing the deposit structure into an acid copper solution resulting in a bi-layer structure, removal of the template, and release of the nanowires facilitated by ultrasonic agitation, followed by a selective copper etch resulting in a multi-scale diameter wire.

Table 3. Electrolyte composition of a (a) Fe-Ni-Mo deposition solution, (b) Cu dipping solution

<table>
<thead>
<tr>
<th>(a) Component</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel (II) sulfate</td>
<td>0.100</td>
</tr>
<tr>
<td>Iron (II) sulfate</td>
<td>0.025</td>
</tr>
<tr>
<td>Sodium Molybdate (VI)</td>
<td>0.016</td>
</tr>
<tr>
<td>Sodium citrate</td>
<td>0.400</td>
</tr>
<tr>
<td>Boric acid</td>
<td>0.500</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>0.001</td>
</tr>
<tr>
<td>Saccharine</td>
<td>0.002</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(b) Component</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper sulfate</td>
<td>0.15</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>0.01</td>
</tr>
<tr>
<td>Sodium citrate</td>
<td>0.45</td>
</tr>
<tr>
<td>Boric acid</td>
<td>0.40</td>
</tr>
</tbody>
</table>
3.4 Cu-Mo-Iron group alloy nanowire

Templated-assisted electrodeposition was carried out in a three-electrode cell with a Pt mesh anode, a saturated calomel reference electrode (SCE) and a nanoporous membrane rendered conductive with a sputtered layer of gold as cathode. Fig. 16 is a schematic of the experimental procedure depicting the preparation of the cathode: a nanoporous polycarbonate membrane (Whatman, porosity <15%, diameter 50 nm) with a ~20 nm sputtered gold thin film (Hummer IV, 15 mA, 70 mTorr, 5 min) on one side. The Fe-Ni-Mo nanowire is pulse electrodeposited, partially or fully filling up the nanopores (Fig. 16a), with the deposition conditions of ≈0.6 V vs SCE for 2 s and -1.4 V vs SCE for 2 s utilizing the following electrolyte: 0.72 M nickel sulfamate, 0.155 M iron sulfate, 0.016 M cobalt sulfate, 0.5 M boric acid, 0.001 M sodium lauryl sulfate, and 0.011 M ascorbic acid, at 40 °C. Following deposition, the partially filled template is dipped into a low pH 1, copper-citrate solution, pH of 1, containing copper ions to induce dealloying and simultaneous displacement of the Fe-Ni-Mo nanowire for 2 min (Fig. 16b). The electrolyte composition of the copper-citrate solution consisted of 0.15 M copper sulfate, 0.45 M sodium citrate,
0.01 M sodium sulfate, and 0.4 M boric acid. The template was then removed through washing in dichloromethane three times (Fig. 16c). Separated nanowires were harvested with ultrasonic agitation for future inspection (Fig. 16d).

The nanowire composition was examined with x-ray fluorescence (XRF) (Kevex, Omicron) and with energy dispersive X-ray spectroscopy (EDS) in a field emission scanning electron microscope (FE-SEM, Hitachi-4800). XRF was used to characterize the average nanowire composition, from top to bottom of the wire, over an array of nanowires. EDS was used to determine, locally the nanowire composition.

The nanowire morphology and structure were inspected with FE-SEM and transmission electron microscopy (TEM). For SEM analyses, the released wires were placed on a plastic surface and covered with a thin sputtered layer of gold for a conductive contact necessary for imaging. Released wires were also imaged with both a low resolution TEM (JEOL JEM-1010) and high resolution TEM (JEOL JEM-2010F); selected-area electron diffraction (SAED), was used to examine the local structure.
Figure 16. Bi-segmented Cu-Mo-iron group nanowires fabrication procedure. (a) electrodeposit Fe-Ni-Mo into a gold-sputtered membrane, (b) exposure of the membrane containing the deposit structure into an acid copper solution resulting in a bilayer structure, (c) removal of the template, and (d) release of the nanowires facilitated by ultrasonic agitation.

3.5 Gold coated nanowire and alignment

As fabricated Fe-Ni-Co nanowires with a thinned region was dipped into a gold solution (AT8000, Technic Inc., operating at a slightly alkaline pH) for 10 min, Since the standard equilibrium potential for Au⁺/Au was much higher than both Cu²⁺/Cu and iron-group elements (Fe, Ni, Co), there will be a electroless deposition of the gold on top of the substrate nanowires (Figure 17). The gold coated nanowires were subsequently cleaned with deionized ultra-filtered water for following SEM and
EDS analysis.

**Etching**

**Dipping in Au solution**

\[ 2\text{Au}^{2+} + 2\text{Cu} \rightarrow 2\text{Cu}^{2+} + \text{Au} \downarrow \]

\[ \text{Au}^{2+} + \text{Fe}_x\text{Ni}_y\text{Co}_z \rightarrow x\text{Fe}^{2+} + y\text{Ni}^{2+} + z\text{Co}^{2+} + \text{Au} \downarrow \]

Figure 17. Fe-Ni-Co nanowire with Cu-Fe-Ni-Co thinned segment was fabricated according to the same conditions as mentioned in section 3.4. The released Fe-Ni-Co nanowires were dipping in Au solution for certain time for electroless deposition.

The final application of this project is to integrate the nanowires with either nanotips or thinned region with a nanofluidic device to detect small biomolecules, therefore, the integration of nanowires with a nanofluidic system is another critical section. Presented here is a section on magnetic alignment of the nanowires using a method that takes advantage of a micron-sized film, or aligned nanowires arrays acting as magnetic anchor, while at the same time, a strong magnetic field is applied to rotate the ferromagnetic nanowires into place.
4 THEORETICAL KMC MODELING

4.1 KMC simulation of metal ion penetration

The Fe-Ni-Co alloy used in the experiments contains only a few wt % Co so
the modeling approach has been simplified to assume that Co ~ 0, and models a Fe-Ni
system, with an initial alloy composition of 71 wt% of Fe, and 29 wt% of Ni. The
KMC simulation in this project contains two section, 1) Cu(II) ions penetrate into the
Fe-Ni alloy with the help of dealloying, 2) thinning of Cu-Fe-Ni porous nanowires
from the result of the former step.

A general flow-chart for KMC simulation of Cu(II) penetrates into Fe-Ni
system is shown in Figure 18, and the algorithm proceeded as follows:

1) Enumerate all the metal atoms generated by randomly assignments of the
materials. Fe-Ni atoms were arranged in a bcc (110) plane manner, and the
system default was periodic along the x-axis and y-axis.

2) Calculate all the possible rates of activated Fe and Ni atoms (atoms that
are located at the surface) using an Arrhenius equation:

\[ r_{diss} = u_{diss} e^{\frac{E_{diss}}{k_B T}}; \quad r_{disp} = u_{disp} e^{\frac{E_{disp}}{k_B T}}; \quad r_{diff} = u_{diff} e^{\frac{E_{diff}}{k_B T}} \]  

(2)
where:

\[ r_{diss} \], represents the dissolution rate for Fe and Ni atoms,

\[ r_{disp} \], represents the displacement rate for Fe and Ni atoms,

\[ r_{diff} \], \( 1 \times 10^{13} / \text{s} \) represents the oscillation frequency for Cu atom diffusion,

\[ v_{diss} \], represents the oscillation frequency for Fe and Ni atom dissolution,

\[ v_{disp} \], represents the oscillation frequency for Fe and Ni atom displacement,

\[ v_{diff} \], represents the oscillation frequency for dissolution [122],

\[ E_{diss} \], represents the dissolution energy barrier for Fe and Ni atoms,

\[ E_{disp} \], represents the displacement energy barrier for Fe and Ni atoms,

\[ E_{diff} \], represents the diffusion energy barrier for Cu atoms,

\[ k_b \], represents the Boltzmann constant,

\[ T \], represents the temperature,

3) Determine the probabilities for every single event to happen by:

\[ P_i = \frac{r_i}{r_{total}} \] (3)
where:

\[ r_i, \text{ represents dissolution rate, displacement rate or diffusion rate,} \]

\[ r_{total}, \text{ represents the summarization of all the rates,} \]

4) Put all probabilities in a list, therefore the sum of this list then generates a random number, \( \mu_1 \), between 0 to 1, the picked event is the one \( S_{i-1} < \mu_1 < S_{i-1} + r_i \), where \( S_{i-1} \) is the probability summarization of the initial \( i-1 \) events.

5) Check whether the condition trigger terminates, there are two factors that both will initiation the jump out of the “for” loop, the first factor is time, which was calculated according to:

\[
\begin{align*}
    t_i &= \frac{-\ln(\mu_2)}{r_{total}} \\
    \text{(4)}
\end{align*}
\]

if \( \text{sum}(t_i) \) is bigger than the cut-off time (e.g. 2 min) the algorithm will jump out of the loop and outputs the results, otherwise it goes to the next step. The second trigger is the step limitation, where the total number of cycling times reach the cut-off default value, then jumps out the loop, and outputs the results.
6) Check whether the algorithm was trapped at a local minimum by
monitoring how much time the same atom was selected during the last ten
cycling. If a single atom was chosen for more than a certain time, the
algorithm was considered trapped at a local minimum, then executes a
“jump to local minimum” process, for other cases, going back to step 2).

7) The “jump to local minimum” step was designed to avoid the algorithm
being trapped at a local minimum for a long time, and induces a low
efficiency. The method is a statistic of all the vacancy energy barriers in
the k-th nearest neighbors of the “trapped” atom, that move the trapped
atom to the vacancy with the highest energy barrier, in other words more
stable. After this step, return to step 2) and start the next cycle.
For Fe-Ni dealloying, the KMC simulation in this project assumes only the first nearest neighbors are taken into consideration. The bonding energies between Fe, Ni, Cu, and vacancy (electrolyte) were estimated following a similar procedure as Erlebacher,[122] and Policastro et al.[123], and listed in Table 4. Therefore, the dissolution energy barrier and displacement energy barrier for Fe and Ni atoms $E_{diss}$, $E_{disp}$, diffusion energy barrier $E_{diff}$, can be calculated as:
\[ E_{\text{Fe-dissolution}} = f_{\text{Fe}} E_{\text{Fe-Fe}} + f_{\text{Ni}} E_{\text{Fe-Ni}} + f_{\text{Cu}} E_{\text{Fe-Cu}} + f_{\text{vacancy}} E_{\text{Fe-vacancy}} \]  

where:

- \( f_{\text{Fe}} \), represents the frequency of Fe atoms in the first nearest neighbors,
- \( f_{\text{Ni}} \), represents the frequency of Ni atoms in the first nearest neighbors,
- \( f_{\text{Cu}} \), represents the frequency of Cu atoms in the first nearest neighbors,
- \( f_{\text{vacancy}} \), represents the frequency of vacancy in the first nearest neighbors,

similarly get all the expressions for: \( E_{\text{Fe-dissolution}} \), \( E_{\text{Ni-dissolution}} \), \( E_{\text{Fe-displacement}} \), \( E_{\text{Ni-displacement}} \), \( E_{\text{Fe-diffusion}} \), \( E_{\text{Ni-diffusion}} \), \( E_{\text{Cu-diffusion}} \).
Table 4. Bonding energies for different metal atoms and electrolyte

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Energy per bond (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Fe</td>
<td>-0.357[124]</td>
</tr>
<tr>
<td>Ni-Ni</td>
<td>-0.371[124]</td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>-0.295[125]</td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>-0.228[126]</td>
</tr>
<tr>
<td>Fe-Cu</td>
<td>-0.133[127]</td>
</tr>
<tr>
<td>Ni-Cu</td>
<td>-0.133</td>
</tr>
<tr>
<td>Fe-Vacancy</td>
<td>0.770</td>
</tr>
<tr>
<td>Ni-Vacancy</td>
<td>0.770</td>
</tr>
<tr>
<td>Cu-Vacancy</td>
<td>0.210</td>
</tr>
</tbody>
</table>

4.2 KMC simulation of Cu-Fe-Ni nanowire thinning

The initial Cu-Fe-Ni structure and atom state is generated as a result of the former step. One modification before running the KMC simulation is to expose the “edge atoms”, which in the Cu(II) penetration process are blocked by the template.
(period condition of x-axis and y-axis) to the surface state. In the Cu-Fe-Ni nanowires
the thinning KMC simulation process, Fe and Ni atoms are passivated, therefore are
only allowed to have surface diffusion. In contrast, Cu atoms will be dissolved.

Therefore, the reaction rates are calculated according to:

\[ r_{\text{diss}} = v_{\text{diss}}e^{\frac{E_{\text{diss}}}{k_BT}}; \quad r_{\text{diff}} = v_{\text{diff}}e^{\frac{E_{\text{diff}}}{k_BT}} \]  \hspace{0.5cm} (6)

where:

\[ E_{\text{Cu-dissolution}} = f_{\text{Fe}}E_{\text{Fe-Cu}} + f_{\text{Ni}}E_{\text{Ni-Cu}} + f_{\text{Cu}}E_{\text{Cu-Cu}} + f_{\text{vacancy}}E_{\text{vacancy-Cu}}, \]

represents the dissolution energy barrier for Cu atoms,

\[ E_{\text{Fe-dissolution}} = f_{\text{Fe}}E_{\text{Fe-Fe}} + f_{\text{Ni}}E_{\text{Fe-Ni}} + f_{\text{Cu}}E_{\text{Fe-Cu}} + f_{\text{vacancy}}E_{\text{Fe-vacancy}}, \]

represents the diffusion energy barrier for Fe atoms,

\[ E_{\text{Ni-dissolution}} = f_{\text{Fe}}E_{\text{Fe-Ni}} + f_{\text{Ni}}E_{\text{Ni-Ni}} + f_{\text{Cu}}E_{\text{Ni-Cu}} + f_{\text{vacancy}}E_{\text{Ni-vacancy}}, \]

represents the diffusion energy barrier for Ni atoms.
5 RESULTS AND DISCUSSION

The conditions to develop the Fe-Ni-Co nanotips, Fe-Ni-Co nanowires with thinned regions, Cu-Mo-Iron group alloy nanowires and the KMC simulation of the Cu(II) ion penetration into Fe-Ni-Co nanowires are addressed in this section.

5.1 Fe-Ni-Co nanotips

Electrodeposition conditions to fabricate nanowires using nanoporous templates have been widely examined for different applications, and several good reviews summarize the vast number of metal and alloy nanowire systems considered [128-131]. Different nanowire morphologies have been reported, some directly formed within the templates, such as nanotubes [132-134], and those that are subsequently etched once released from their templates, such as nanogaps [131, 135], and porous nanowires [81, 82], or through subsequent annealing or displacement reactions resulting in interesting structures, such as nanopeapods [136, 137].

In this research, an electrodeposition/anodization approach is presented to generate a nanowire with a nanotip. The tip is generated from the middle layer of a multilayered nanowire deposit upon etching. The conditions to fabricate the
nanowires are presented, with an analysis of the controlling phenomenon that govern deposition, oxidation and subsequent reduction of the oxide in creating a novel interfacial region that etches into a tip form.

5.1.1 Thin film and polarization

Kim et al. [138] reported conditions for the electrodeposition of Fe-rich, Fe-Ni-Co alloys with a similar electrolyte used here, where the resulting deposit composition was comparable to Super Invar, 64 wt % Fe, 31 wt % Ni, 5 wt % Co, under DC conditions from -20 mA/cm² to -60 mA/cm². In order to ensure kinetic conditions where the deposit composition does not change with different mixing environments, important to nanowire growth, deposits were examined using the RCE at different current densities and rotation rates. Figure 19 shows the influence of varying the deposit applied current density (Figure 19a-c) and electrode rotation rate (Figure 19d-f) on the deposit composition (Figure 19a, d), and the corresponding cathodic current efficiency (Figure 19b,e). Using this data, the steady state, partial current densities are determined in Figure 19c and Figure 19f for changes in applied current density and rotation rate, respectively. In Figure 19a, the composition changes
significantly with the applied current density, increasing in iron deposit content. In contrast, Kim et al.\cite{138} reported that the composition did not change above -15 mA/cm$^2$, but a significant difference here is that the rotation rate of the electrode is higher. In Figure 19b, the current efficiency is very low at -15 mA/cm$^2$ but then jumps to a higher range that does not change appreciable with the applied current density. The partial current densities of the all the metal reduction rates, shown in Figure 19c, gradually increases with the applied current density indicative of a kinetic control. The limiting current density can be estimated, assuming a boundary layer determined from the Eisenburg relation for a RCE \cite{139}

$$i_{lim} = \frac{-nFE^b}{\delta}; \quad \delta = 99.62d^{-0.4}v^{0.344}D^{0.356}S^{-0.7}$$

(7)

where:

- $\delta$, represents the Nernst diffusion layer thickness,
- $d$, 1 cm represents the electrode diameter,
- $v$, 0.01 cm$^2$ s$^{-1}$ represents the kinematic viscosity,
- $S$, 1000 rpm represents the electrode rotation rate,
- $D$, $5.0 \times 10^{-6}$ cm$^2$s$^{-1}$ represents a constant diffusion coefficient,
Estimates of the limiting current density for each reactant are -330 mA/cm$^2$, -71 mA/cm$^2$, and -3 mA/cm$^2$ for nickel, iron, and cobalt ions, respectively for a 21 µm boundary layer. In Figure 19c, the Fe and Ni partial current densities at all applied current densities are an order of magnitude lower than their expected limiting current densities and clearly have not reached their mass transport limit. Despite the low concentration of Co$^{2+}$, the Co partial current density has not reached its limiting current density. In the polycarbonate nanotemplate used here, the depth of the template is 6 µm with additional stirring in the electrolyte, thus a boundary layer on the order of 10 µm outside of the template, with an estimate of the total boundary layer ~ 16 µm, similar to the magnitude of the boundary layer established by the RCE. To ensure that the deposit composition would not be altered with a change in boundary layer, a variation in rotation rate was examined.
Figure 19. Fe-Ni-Co RCE thin film galvanostatic deposition (a,b,c) at a constant rotation rate, 1000 rpm, and (d,e,f) at a constant applied current density $-50$ mA/cm$^2$; (a,d) composition (b,e) corresponding current efficiency and (c,f) partial current densities.

Figure 19d-f shows results of the Fe-Ni-Co thin film electrodeposits fabricated at $-50$ mA/cm$^2$ at different rotation rates. On the x-axis, the rotation rate has been scaled to the 0.7 power, since reactions under a mass transport limited control on cylinders should follow this functionality, according to Eq 7. The deposit composition
(Figure 19d) shows no significant change with respect to variations in rotation rate, and thus the composition in the growing nanowire should remain constant. The current efficiency (Figure 19e), however, demonstrates a significant decrease as rotation rate increases. Unexpectedly, the metal partial current densities decrease when the rotation rate increases, thus the rate of deposition inside the nanoporous membranes can change with the growing metal. However, the composition remains the same, as the change of the partial current densities occur in the same ratio. The side reaction, hydrogen evolution, however increases with rotation rate (Figure 19f), which suggests that as the nanowires grow and the effective boundary layer thickness for the proton decreases, the current efficiency may become progressively worse. Due to this hydrogen evolving side reaction, the deposit was pulse deposited into the nanoporous templates in order to avoid entrapped gas bubbles.
Figure 20. RCE polarization curves on Fe-Ni-Co thin films fabricated at -50 mA/cm² in a Fe-Ni-Co electrolyte polarized in the (a) cathodic direction at different rpms, (b) anodic direction at different pHs, rotation rate: 1000 rpm.

Figure 20 are polarization curves at 1000 rpm for Fe-Ni-Co thin films fabricated at -50 mA/cm², in both the cathodic (Figure 20a) and anodic (Figure 20b) regions with the same Fe-Ni-Co electrolyte used for its deposition. In Figure 20a the rotation rate is varied. The peaks near -0.8 V to -0.9 V vs SCE are attributed, in part, to the transient behavior of the proton reduction mass transport control. Also prior to the polarization curve, the Fe-Ni-Co film was exposed to the air, where a native oxide is expected, and the peaks may also be due to the reduction of an Fe-rich oxide.

Figure 20b shows the anodic RCE polarization curves of Fe-Ni-Co thin films deposited at -50 mA/cm² in a pH 2 and 5, Fe-Ni-Co electrolyte to map out conditions where oxides are evident. The Fe-Ni-Co film shows no obvious passivation in the pH
2 Fe-Ni-Co electrolyte throughout -0.4 V to 0.5 V vs SCE, but a clear passivation region between -0.4 V vs SCE and 0.3 V vs SCE at a pH of 5 occurs. Therefore, if the local pH change during nanowire fabrication is minimal then at the open circuit potential (OCP) condition, or with an impressed positive overpotential, no oxide film formation would be expected in the pH 2 deposition electrolyte, although at higher pH, such as pH 5, it is possible to passivate the surface with a small anodic overpotential.

5.1.2 Nanowires

Figure 21 shows the resulting potential and current transient curves during the three different nanowire fabrication steps, as depicted in Figure 18. Figure 21a shows the potential transient when using a pulse galvanostatic deposition for the first Fe-Ni-Co segment. In Figure 21b, the anodic current density transient values are presented for variable applied potentials, and in Figure 21c the potential transients that occur during the top Fe-Ni-Co layer deposition again by a pulse cathodic current density, that follows the different previous anodic applied potentials. During the first, bottom layer of Fe-Ni-Co, in Figure 21a, there is an initial stage where an “on” potential at -0.95 V vs SCE remains relatively constant until approximately 200 s
(with a fresh Fe-Ni-Co solution) or 330 s (with an aged Fe-Ni-Co solution) and the “off” potential reaches -0.6 V vs SCE. If the deposition is terminated during this initial stage and the membrane dissolved, no nanowires were observed. It was critical that the deposition time needed to exceed this initial stage for nanowires to be confirmed. Because this region is affected by the aging of the electrolyte, and thus formation of Fe$^{3+}$, the reduction of Fe$^{3+}$ to Fe$^{2+}$ is the expected reaction. After this initial stage, the “on” potential is between -1.15 and -1.18 V vs SCE and nanowires are formed, while the “off” potential remains near -0.6 V vs SCE.

An intermediate oxide layer was anodically deposited and the generated current transients are similar to the ones reported by Wu and Lee [140] for iron oxide. Initially there is a nucleation stage, with a characteristic drop in current density followed by an increase in current density as the nuclei grow and their diffusion zones start to overlap, where they found a transition of nanorod growth to nanosheets, thus an aggregation of nuclei. At small, anodic overpotentials (0.1 V vs OCP, Figure 21b, inset) the current density does not significantly increase indicating that there is no significant overlapping effect. At 0.2 V vs OCP, there is some overlapping effect, and
possible aggregation of nuclei, and at even larger overpotential the initial nuclei are expected to be smaller and more numerous. Figure 21c shows the potential changes following the anodization steps in Figure 21b, generated by a pulse cathodic current deposition. Of particular interest is the potential changes at the beginning stage. Initially, when a cathodic current is applied the “on” potential reaches -1.15 V vs SCE if the step before it had no anodic treatment, or had a low anodic overpotential, similar to the initial deposition of the first part of the nanowires in (Figure 21a). If a large anodic overpotential is applied at step 2 and is followed by the reduction step, the potential first reaches -0.85 V vs SCE, and this region is extended in time with larger overpotentials. Thus, in this region the reduction of the generated oxide is expected. In the polarization curves (Figure 20a), an inflection occurs near the same potential range, ~ -0.85 V vs SCE, for all samples due to the proton reduction side reaction at a pH of 2, and reduction of surface oxide. Since there is an expected local pH rise occurring in the nanoporous template, in contrast to the thin film deposition, this potential response occurring within the nanoporous template, should reflect the reduction of the oxide generated from step 2.
Figure 21. Potential and current transients during nanowire fabrication, (a) Fe-Ni-Co pulse cathodic current deposition (step 1), (b) anodization by different applied anodic potentials (step 2), and (c) Fe-Ni-Co pulse cathodic current following the previous anodization treatment (step 3).
Figure 22 shows TEM and SAED results for representative tri-layered nanowires released from their templates when the applied anodization potentials for the second layer had a value of +0.4 V vs OCP for 10 s. Without any subsequent etching step, all the nanowires are continuous. Figure 22a shows a low magnification image of the released nanowires, and Figure 22b is a high magnification image of the interfacial region, which was produced by reducing the iron-rich oxide created during the oxidation step; however, the boundary between the layers is not sharp. SAED results of the reduced oxide region is depicted in Figure 22c indicates a polycrystalline structure, while in Figure 22d the Fe-Ni-Co alloy region has a SAED result with less discrete points, and a more amorphous structure.

Figure 22. TEM images of nanowires fabricated with the intermediate, second layer deposited at an applied potential of 0.4 V vs OCP before etching; (a) low and (b) higher magnification. SAED results for the (c) oxide region that was reduced and (d) Fe-Ni-Co region.
5.1.3 Nanotips

After the wires are released, they are then exposed to the etching solution. The interfacial region, created at the end of step 1 and during step 2, is etched in a non-uniform manner. This is the region that is more crystalline. The rest of the nanowires, deposited by using the pulse cathodic current, does not significantly change its size. Once etched, either a gap or a nanotip is observed (Figure 23) at the region where the anodic potential was applied. When there is no applied anodic potential, at the OCP, a gap structure is generated after etching (Figure 23a), with a gap size around 10 nm. As the anodic potential increases from 0.1 V vs OCP to 0.6 V vs OCP, there is an evolution of nanotip structures fabricated as shown through Figures 23b to f. The tip size is roughly 10 times smaller than the wire diameter. Since the tri-layered nanowires were deliberately fabricated with a longer first layer of Fe-Ni-Co and shorter second layer of Fe-Ni-Co by manipulating the deposition time, it’s easy to identify the direction of the tip. They occur pointing in the direction toward the first, longer Fe-Ni-Co layer.
Figure 23. Nanotips fabricated by etching nanowires in a pH 5 citrate-boric solution. Evolution of nanotips structure (a-f) with an increase in overpotential (0 V vs OCP – 0.6 V vs OCP).

Figure 24. Nanotips structure fabricated with the anodic potential of 0.2 V vs OCP and etched without agitation (a) low magnitude image, (b) high magnitude image.

Electrolyte agitation was important in how the interfacial nanowire region was reacted. In Figure 24, the applied anodic potential of the inner, oxide region was 0.2 V vs OCP, and the etching step used to create the nanotips was completed within a stationary electrolyte for 10 min to compare with the results in Figure 23c. Without
electrolyte agitation, the wire interfacial region and the second Fe-Ni-Co layer was significantly affected. Without electrolyte agitation, a more porous surface structure is generated during the etching step, which is suspected to be facilitated by the mass transport control of dissolved oxygen. Also note, that the other side of the tip is connected to the first layer, or bottom Fe-Ni-Co that is not porous.

The development of the tip structure may be related to changes of crystallinity, porosity and composition at the interfacial region, between the deposit formed at the end of step 1 and at the beginning of step 2, which is created by reducing an oxide between two Fe-Ni-Co layers. Upon etching, the intermediate, second layer has a more crystalline structure that is etched non-uniformly creating the tips. Many amorphous materials display excellent corrosion resistance in comparison with their crystalline counterparts, such as polycrystalline iron oxide [141], nickel [142], zinc, [143] and steal [144]. Therefore, the preferential etching of the more crystalline region, generated by oxide and then reducing it, is expected to be more prone to etching compared to the rest of the wire.

Monteiro et al. [145] studied magnetite reduction in a strong alkaline
electrolyte and indicated that there is a gradual development of porosity at the magnetite/bulk electrolyte interface. Thus, as the oxide is reduced the product, being either a Fe(II) oxide or Fe$^{2+}$ ion would result in a lower porosity. A significant difference between this study and the one presented here is that as the oxide is reduced, creating a porous structure, in the work here, metal is also reduced at the same time. So unlike the oxide studies by Monteiro et al., the porosity would be expected to be smaller as the pores are also filled by the depositing metal. Additionally, during the filling of a porous structure from the top region of the wire within the template downwards, a gradient in porosity can develop. After the release of the wires, the non-uniform dissolution of the metal alloy in the radial direction is thought to be formed by such a distribution of porosity, where there is more porosity near the interfacial region where the first Fe-Ni-Co/reduced oxide layer is created and less porosity at the reduced oxide/last Fe-Ni-Co layer. In addition, the gradient in porosity and size of the crystallites that results from the reduced oxide is expected when the oxide nuclei number is large, hence at high overpotential. When there is a smaller number of nuclei, at low anodic overpotential, the resulting structure after it is
reduced is expected to have larger grains and less distribution of porosity, and in this case the tip is less refined.

Fe oxide stability is expected for high pH electrolytes. Schmuki et al. [146] studied the reduction of iron oxides at different pH values: 1.6, 8.4 and 11.7. In an acidic electrolyte (0.1 M H$_2$SO$_4$), chemical dissolution of the surface oxide layer results in the dissolution of the oxide to Fe$^{2+}$. However, in an alkaline electrolyte (0.1 M NaOH), the reduction reaction of Fe oxide undergoes a solid-state transformation Fe$_2$O$_3$ → Fe$_3$O$_4$ reducing the oxidation state of iron from 3 to 2.67, at a high pH. Interestingly, the pulse transition potential results shown in Figure 21c with large overpotentials exhibits a similar transient behavior as Schmuki’s pH 8.4 case (borate) during a non-pulse, reduction under constant current. For this intermediate pH condition, both a solid state transformation Fe$_2$O$_3$ → Fe$_3$O$_4$ and dissolution, Fe$_3$O$_4$ → Fe$^{2+}$ were found to both occur at a potential region that is near -0.8 V vs SCE until all the oxide was reduced. This value corresponds well with the one observed here in the initial part of the transient in Figure 21c, for the reduction of the Fe-rich oxide generated from step 2. As the pulse “on” potential becomes more negative in Figure
21c, during the applied cathodic current, a combination of oxide reduction and Fe-Ni-Co deposition occurs from -0.85 V vs SCE to -1.15 V vs SCE particularly when there is a larger applied overpotential used to generate the oxide in step 2. An indication when all the oxide during step 2 is reduced occurred when the pulse “on” potential in Figure 21c reaches the same value as during the first part of the reduction of the Fe-Ni-Co nanowires, Figure 21a.

Compositional difference can also account for changes in corrosion. For example, Leith and Schwartz [147] showed that a micro-sized structure containing Fe-rich Fe-Ni alloys can be preferentially etched compared to Ni-rich alloys in acid. The Ni-rich region (75%) were those that were corrosion resistant. The local, nanoscale composition along the nanowires were not inspected here, however, based on the potential values recorded during nanowire deposition and compared to our thin film deposition, the compositional changes can be inferred. At the interfacial region where the nanotip develops, as the oxide reduces and the alloy deposits, the potential changes from -0.85 V vs SCE to -1 V vs SCE. In thin film deposits fabricated at -15 mA/cm² (Figure 19a), the composition corresponded to a value 55 wt % nickel,
(Figure 20, -0.85 V vs SCE) and drops to 30 wt % nickel at -50 mA/cm$^2$ at the less noble potentials, (Figure 20, -1.1 V vs SCE). Thus, the thin film deposition data can serve as an estimate of the largest anticipated composition change at the interfacial region where the tip occurs. The nickel range in this case is still fairly rich in iron which would be susceptible to corrosion. Additionally, if there was indeed a nickel/iron concentration gradient in the nanowires, they would have slightly more nickel near the interface of the 1$^{st}$ and 2$^{nd}$ layer, but this is the region that etches the most, not the least. Therefore, the preferential etching of the presented nanowires in forming a tip is not expected to be due to composition changes.

Figure 25 summarizes the conditions that lead up to forming nanotip structures after etching. Fe-Ni-Co segments are first pulse electrodeposited together with proton reduction, step 1, increasing the local pH (Figure 25a) enough for the stabilization of an oxide at the start of step 2. Applying an anodic potential, an iron-rich oxide layer is expected to deposit (Figure 25b). Due to the existence of the oxide layer, the following application of a pulse current can be split into three stages: first, at the beginning of step 3 (Figure 25c), the iron-rich oxide starts to reduce while at the same
time the Fe-Ni-Co alloy is deposited, both at a potential near -0.85 V vs SCE. As the oxide is continuously consumed, the metal ions may encounter mass transport limitations at the edge of the oxide layer due to the deposition reducing the oxide porosity. A gradient porous region is generated in situ of the original oxide region (Figure 25d). After all the oxide is reduced, the corresponding potential decreases to -1.15 V vs SCE, and the second layer of Fe-Ni-Co starts to grow. This layered nanowire, now having a middle layer with a different crystalline structure and porosity is then subsequently etched and produces nanotips.
Figure 25. Schematic illustrating the progression of the electrochemically fabricated multilayered nanowires with embedded porous regions as a precursor for nanotips with corresponding potential transients. (a) pulse deposition of the first layer of Fe-Ni-Co, (b) an oxide layer was generated through an applied cathodic potential, (c) an immediate pulsing deposition was applied after the oxide layer to reduce the oxide and deposit Fe-Ni-Co simultaneous, (e) growth of the second layer Fe-Ni-Co.

5.2 Fe-Ni-Co nanogaps with electrodeposited Cu as sacrificial layer

5.2.1 RCE experiments on Fe-Ni-Co and Cu

To survey conditions to etch either chemically or electrochemically in a citrate solution, polarization curves were examined. A rotating cylinder set-up was used so that the hydrodynamic environment near the electrode surface can be well maintained.
Figure 26 shows the experimental set-up and a representative set of polarization curves on a large rotating cylinder electrode (d = 1 cm) covered with the Fe-Ni-Co deposited at -50 mA/cm$^2$ at 40 °C at a rotation rate of 1000 rpm. The resulting deposit composition was examined with x-ray fluorescence: 63 wt % Fe, 35 wt % Ni, and 2 wt % Co. The cylinders were electrochemically etched in a citrate-boric acid electrolyte (0.01 M sodium sulfate, 0.45 M sodium citrate, and 0.40 M boric acid). The resulting pH was 7.5 and sulfuric acid was used to lower the pH to 5. In Figure 26a a three electrodes cell design was used so that the potential of the working electrode can be identified where Fe-Ni-Co can be passivated and etched. Figure 26b shows that the pH of the etchant changes slightly the open circuit potential from -0.55 to 0.42 V vs SCE from low to high pH. Also, the higher the pH the more passivated the Fe-Ni-Co becomes, decreasing its etching rate.
Figure 26. The rotating cylinder working electrode (a) apparatus and (b) resulting polarization curves of a Fe-Ni-Co deposit fabricated at –50 mA/cm² being anodized in a citrate acid electrolyte at different pH, scan rate = 2 mV/s.

Copper was chosen as a sacrificial material to generate the nanogap ultimately in the nanowires. Polarization curves of Cu etching were first examined on the RCE. Figure 27 shows a comparison of the Cu etching in the same electrolyte with pH from 4 to 7. The desirable etching condition is then one where the Fe-Ni-Co is protected through the formation of a passivating oxide and where Cu is not protected and can be anodized at a high rate. Thus to meet these two criteria a potential of 0.4 V vs SCE and a pH of 5 was chosen for this etching electrolyte.
Figure 27. Polarization curves of a Cu being anodized in a citrate-boric acid electrolyte at different pH, scan rate=2 mV/s.

5.2.2 Fe-Ni-Co nanogaps fabrication

According to Faraday’s Law, Eq 8, the charge passed is directly proportional to the mass deposited if the current efficiency remains constant. Therefore, different Cu deposition times were examined.

\[
L = \frac{M \cdot \int i \, dt}{nF \cdot \rho} \tag{8}
\]

where:

- \( M \), represents molar mass of the substance (g/mol)
- \( i \), represents current density (A/cm\(^2\))
$t$, represents total time the constant current was applied (s)

$\rho$, represents density of Cu (g/cm$^3$)

$F$, 96485 A s/mol represents Faraday’s constant

$n$, represents electrons transfer per ion (equiv/mol)

$L$, represents length of nanowires growth in the membrane (cm)

$\epsilon$, represents current efficiency

Figure 28 shows Fe-Ni-Co/Cu/Fe-Ni-Co nanogaps with Cu fabricated by electrodeposition for a certain time. The copper deposition time used in Figure 28a, Figure 28b, and Figure 28c, was 50 s, 10 s, and 0.02 s, and the resulting gaps sizes after the Cu was etched away were 700 nm, 600 nm, and 500 nm, respectively. Since the deposition time should be directly proportional to the amount of copper deposited, subsequent etching was expected to yield proportionally smaller gaps as the time was decreased. The gaps shown in Figure 28 do not change by an order of magnitude, despite the change of the deposition time on Eq 8, theoretical lengths should be no larger than 55 nm, 11nm and 0.022 nm, which were obtained at 100% current efficiency, respectively. The disparity between the theoretical and practical gap sizes
values can be attributed in part to the discrepancy in the porosity used, because Whatman Inc. reports a very wide porosity range [148]. Thus, 10% porosity may be higher than the real porosity. But it is worth it to note that the nanogaps in Figure 28c theoretically should be 2500 times smaller than nanogaps in Figure 28c. This result suggested that something is unaccounted for: either there is an electroless component of the Cu electrodeposition that is creating larger thicknesses than anticipated, or that during etching a part of the Fe-Ni-Co alloy is also being dissolved, or that simply the wires tend to break apart and move to create larger gaps. To overcome this problem, an electroless deposition method using chemical displacement was developed to prepare small gap sizes, which will be discussed in chapter 4.3. The electroless approach can also help to identify if the Fe-Ni-Co region is also being etched, depending if small gaps are indeed obtained.
Fe-Ni-Co nanogaps fabricated with electrodeposited Cu as the sacrificial layer, copper layer was electrodeposited at \(-3\) mA/cm\(^2\) for (a) 50 sec, (b) 10 sec, and (c) 0.02 sec. The Fe-Ni-Co/Cu/Fe-Ni-Co tri-layered nanowires were etched electrochemically at 0.4 V vs OCP for 1 min.

5.3 Fe-Ni-Co nanowire with thinned region

Due to the large gaps formed in the previous section, it was evident that the copper displacement reaction occurred not just at the Fe-Ni-Co nanowire surface but within the nanowire. Therefore, this effect was used to create regions on the nanowire that could be etched to subsequently create thinned regions. Displacement reactions involving a more noble elemental ion that is reduced at the expense of anodizing a less noble material can cover the surface of the less noble material in a self-limiting way. Recently, displacement accompanied by interstitial solid state diffusion, has been shown to form unique structures at the nano-scale [69-71]. The initial displacement reaction can generate a thin layer of a noble material at the surface of a less noble
substrate, however, surface pinholes allow the reaction to continue into the less noble solid structure resulting in hollow or porous nano-architectures.

In this research, a method that combines Fe-Ni-Co electrodeposition, coupled Cu displacement and Fe dealloying, followed by a selective etch of Cu is used to create thinned nanowire regions or gaps. An iron-rich alloy composition is chosen to allow for the expected dealloying of the nanowire when it is exposed to an acid electrolyte, and for its passivation characteristics that are important to protect a part of the nanowire during the final etching step. The Cu displacement, and dealloying via corrosion reactions, are coupled and occur simultaneously to create a reaction front that propagates axially along the electrodeposited nanowire and is pH dependent. The electrolyte composition of the displacement step is examined to determine the characteristic behavior of the coupled reactions. Unique to this procedure is that novel Fe-Ni-Co wires with multiscale diameters are connected together; and with the larger diameter being ferromagnetic, they may be of interest to build nanocircuits as they can be magnetically positioned into a device. The presented methodology can also be used as a tool to study the propagation of the displacement reaction into a nanowire.
The SEM image in Figure 29b is a collection of Fe-Ni-Co nanowires, having diameters of 100 nm, that were released from the membrane prior to the copper ion treatment having a composition that is Fe-rich (Figure 29c) from EDS point analysis of three different regions along a nanowire. The image in Figure 29d shows resulting wires that were first electrodeposited in the nanoporous membrane and then dipped into a low, pH 1, copper-citrate solution prior to dissolving the membrane. The electrolyte composition of the copper-citrate solution consisted of copper sulfate (0.15 M), sodium citrate (0.45 M), sodium sulfate (0.01 M), and boric acid (0.4 M). The conditions combine a Cu displacement reaction with corrosion of the alloy so that the copper ions can penetrate into the electrodeposited alloy. Removing the membrane, a selective area EDS composition analysis confirmed a copper rich composition at the end of the wire indicating that displacement occurred on the end of the wire (Figure 29e). Followed by a 2 min etch in a pH 5 citrate solution, having the following composition: sodium citrate (0.45 M), sodium sulfate (0.01 M), and boric acid (0.4 M). A thin nanowire region is generated where the displacement reaction previously occurred (Figure 29f), leaving behind an alloy that is rich in Cu but with different
proportions of Fe, Ni and Co (Figure 29g). The thinning affect was ascribed primarily to copper dissolution. Also noted, that there was no thinning affect observed if there was no copper ions in the first, dipping solution, making it difficult to track where reactions occurred after the wires were released from the membrane.

Figure 29. (b-e) SEM image of tri-layered Fe-Ni-Co/Cu-Fe-Ni-Co/Fe-Ni-Co nanowires after exposure to the copper-citrate electrolyte with the copper ion concentration 0.15 M, 2 min, at variable pH: 0, 1, 2 and 4. (f) A summary of the penetration length with the proton concentration. Scale bar 1000 nm.

To investigate how far the displacement reaction can propagate into the wire, a third layer of Fe-Ni-Co was electrodeposited over the displaced region. Since the subsequent etch time was constant, the resulting thinned region can have different diameters, or none at all, resulting in a gap, depending on the total mass reacted in the previous displacement reaction. The addition of a third, top layer that sandwiches the
copper rich region between two Fe-Ni-Co layers, as depicted in Figure 30, helps to identify the displaced region even if it is completely etched away. The resulting changes of the middle, copper rich layer is dependent on the solution conditions used in the dipping step after the first Fe-Ni-Co layer is electrodeposited.

5.3.1 Parameters effect during metal ion penetration and thinning

The standard redox potentials of Fe$^{2+}$/Fe° (-0.440 V vs. SHE), Ni$^{2+}$/Ni° (-0.257 V vs. SHE) and Co$^{2+}$/Co° (-0.277 V vs. SHE), are all significantly more negative than H$^+$/H$_2$ (0 V vs. SHE) and Cu$^{2+}$/Cu (0.340 V vs. SHE). Thus, a corrosion reaction due to the presence of protons simultaneously with a copper displacement reaction is expected to occur. A change in pH should influence the copper reaction front into the Fe-rich nanowire due to the corroding alloy (Figure 30) and the concentration of Cu(II) ions should also be expected to affect the region where displacement occurs (Figure 34).
Figure 30. Nanowire tri-segment thinning procedure pH effect on the penetration length. (a) procedure as in Figure 15, with an additional layer of Fe-Ni-Co following the acid copper ion solution treatment. (b-e) SEM image of tri-layered Fe-Ni-Co/Cu-Fe-Ni-Co/Fe-Ni-Co nanowires after exposure to the copper-citrate electrolyte with the copper ion concentration 0.15 M, 2 min, at variable pH: 0, 1, 2 and 4. (f) A summary of the penetration length with the proton concentration. Scale bar 1000 nm.

Figure 30 shows the deposition, displacement/dealloying and etching procedure with tri-layered nanowires having an etched region that is sandwiched between two Fe-Ni-Co segments. The procedure in Figure 30a is similar to Figure 15, but with an additional Fe-Ni-Co layer that sits atop of the copper treated Fe-Ni-Co
wire. An elemental distribution in a collection of tri-layered nanowires before etching was monitored by EDS mapping, shown in Figure 31, that verifies the presence of a Cu-rich region in between two Fe-Ni-Co segments. As depicted in Figure 30b-e, the penetration length of copper ions decreases from 2300 nm to 160 nm when the pH of the copper solution changes from 0 to 4, for a constant etching time. Consequently, long, uniform thin nanowire regions, having diameters that are 5 times thinner or more than the original size nanowires can be fabricated at low pH values of 0 and 1 (Figure 30b,c), while at higher pH values short gaps (Figure 30d,e) are obtained. The length of the alloy nanowire that was reacted is summarized in Figure 30f. At low pH, the copper species are predominately Cu$^{2+}$, and there is high concentration of protons to facilitate corrosion of the alloy, permitting the Cu$^{2+}$ ions to propagate into the nanowire and displace a part of the remaining Fe-Ni-Co solid. At high pH, the reaction front is limited by a lower corrosion reaction due to the low amount of proton, but also the copper species are complexed with citrate ligands, so that the displacement reaction rate is also affected. Copper species with citrate ligands are provided in Figure 32, and simulated according to the equilibrium equations listed in
Figure 31. SEM-EDS mapping for tri-layered Fe-Ni-Co nanowires with intermediate Fe-Ni-Co-Cu thinning segments before etching. (a) Sketch and SEM images for nanowires before etching, Fe-Ni-Co was immersed in Cu(II), pH 1 solution for 2 min. (b-e) EDS analysis for element of Fe, Ni, Co and Cu respectively.
Table 5. Equilibria reactions and corresponding stability constants from citrate solution. (A represents C₆O₆H₄).

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Equilibrium equations</th>
<th>ref.</th>
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<tbody>
<tr>
<td>1 (\text{Cu}^{+2} + \text{OH}^- = \text{CuOH}^+)</td>
<td>(10^{6.3} = \frac{[\text{CuOH}^+]}{[\text{OH}^-][\text{Cu}^{+2}]})</td>
<td>[153]</td>
</tr>
<tr>
<td>2 (\text{Cu}^{+2} + 2\text{OH}^- = \text{CuOH}_2^-)</td>
<td>(10^{12.8} = \frac{[\text{CuOH}_2^-]}{[\text{OH}^-]^2[\text{Cu}^{+2}]})</td>
<td>[153]</td>
</tr>
<tr>
<td>3 (\text{Cu}^{+2} + 3\text{OH}^- = \text{CuOH}_3^-)</td>
<td>(10^{14.5} = \frac{[\text{CuOH}_3^-]}{[\text{OH}^-]^3[\text{Cu}^{+2}]})</td>
<td>[153]</td>
</tr>
<tr>
<td>4 (\text{Cu}^{+2} + 3\text{OH}^- = \text{CuOH}_4^{2-})</td>
<td>(10^{15.6} = \frac{[\text{CuOH}_4^{2-}]}{[\text{OH}^-]^4[\text{Cu}^{+2}]})</td>
<td>[153]</td>
</tr>
<tr>
<td>5 (2\text{Cu}^{+2} + 2\text{AOH}^- = \text{Cu}_2\text{OH}_2^{2-})</td>
<td>(10^{14.43} = \frac{[\text{Cu}_2\text{OH}_2^{2-}]}{[\text{Cu}^{+2}]^2[\text{AOH}^-]^2})</td>
<td>[154, 155]</td>
</tr>
<tr>
<td>6 (\text{Cu}^{+2} + \text{AOH}^- + \text{H}^+ = \text{CuH}(\text{AOH}))</td>
<td>(10^{9.55} = \frac{[\text{CuH(\text{AOH})}]}{[\text{Cu}^{+2}][\text{AOH}^-][\text{H}^+]})</td>
<td>[154, 155]</td>
</tr>
<tr>
<td>7 (2\text{Cu}^{+2} + 2\text{AOH}^- = \text{Cu}_2(\text{AO})_2^{4-} + 2\text{H}^+)</td>
<td>(10^{5.87} = \frac{[\text{Cu}_2(\text{AO})_2^{4-}]}{[\text{Cu}^{+2}]^2[\text{AOH}^-]^2})</td>
<td>[154, 155]</td>
</tr>
<tr>
<td>8 (2\text{Cu}^{+2} + 2\text{AOH}^- = \text{Cu}_2(\text{AOAO})_2^{5-} + \text{H}^+)</td>
<td>(10^{5.85} = \frac{[\text{Cu}_2(\text{AOAO})_2^{5-}]}{[\text{Cu}^{+2}]^2[\text{AOH}^-]^2})</td>
<td>[154, 155]</td>
</tr>
<tr>
<td>9 (2\text{Cu}^{+2} + \text{AOH}^- = \text{Cu}_2\text{AO} + \text{H}^+)</td>
<td>(10^{4.92} = \frac{[\text{H}^+][\text{Cu}_2\text{AO}]}{[\text{Cu}^{+2}]^2[\text{AOH}^-]})</td>
<td>[156, 157]</td>
</tr>
<tr>
<td>10 (\text{H}_2\text{AOH}^- = \text{H}^+ + \text{AOH}^-)</td>
<td>(10^{-6.3} = \frac{[\text{H}^+][\text{HAOH}^-]}{[\text{HAOH}^-]})</td>
<td>[158, 156]</td>
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<tr>
<td>11 (\text{H}_3\text{AOH}^- = \text{H}^+ + \text{H}_2\text{AOH}^-)</td>
<td>(10^{-4.34} = \frac{[\text{H}^+][\text{HAOH}^-]}{[\text{HAOH}^-]})</td>
<td>[154, 155]</td>
</tr>
<tr>
<td>12 (\text{H}_3\text{AOH} = \text{H}^+ + \text{H}_2\text{AOH}^-)</td>
<td>(10^{-2.92} = \frac{[\text{H}^+][\text{H}_2\text{AOH}^-]}{[\text{H}_2\text{AOH}]})</td>
<td>[154, 155]</td>
</tr>
<tr>
<td>13 (\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-)</td>
<td>(10^{-13.92} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]})</td>
<td>[159]</td>
</tr>
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Figure 32. Cu-citrate complex species distribution as a function of solution pH.

Figure 33 provides transmission electron microscopy (TEM, JEOL JEM-1010) and SEM images images of Fe-Ni-Co nanowires before and after they are corroded in a pH 0 solution, not containing copper ions, for 30 s. The proton corrodes Fe-Ni-Co unevenly, near grain boundaries to generate a porous structure. The average composition of the alloy shows that there is an enrichment in Ni and Co, thus a preferential corrosion of Fe, or in other words, dealloying.
Figure 33. Fe-Ni-Co nanowires before and after etching. (a) Sketch before etching, (b-c) TEM and SEM images. (d) EDS analysis. (e) Sketch after etching in a pH 0 boric acid-citrate electrolyte, 30 s. (f-h) TEM and SEM images. (h) EDS analysis.

Figure 34 shows the evolution of the penetration length of the tri-layered wires, as a function of copper concentration in the dipping solution at a constant pH of 1. The penetration length appears as a gap region and/or a thinned region. Figure 34a, the result using a low copper concentration, shows all gapped regions. At higher copper concentration, such as in Figure 34d, the penetration length is given by the length of a thinned region. In Figure 34e, the penetration region is defined by areas that are a combination of gaps and thinned regions. As copper concentration decreases from 2X (Figure 34e) to 1/10X (Figure 34a), where X=0.15 M copper sulfate, the penetration length is reduced in a non-linear manner as summarized in Figure 34f.
Figure 34. Copper concentration effect on penetration length. SEM images of Ni-Fe-Co nanowires after dipping into the copper-citrate electrolyte with varied copper ion concentration of (a) 1/10X, (b) 1/5X, (c) 1/2X, (d) 1X and (e) 2X, X=0.15 M, pH=1, dipping time and etching time 2 min. (f) The summary of the penetration length with copper concentration. Scale bar 1000 nm.

Since both protons and copper species contribute to how far the copper displacement reaction propagates into the nanowires for a given time, the concentration ratio of the proton and copper ion species, \([H^+] / [Cu(II)]\), may be an important design parameter. The resulting etched nanowires formed with the displacement electrolyte containing different ratios of concentration of 0.2, 0.4, 0.8, 1.6, and 3.2 is presented in Figure 35a-e. The bulk concentration of proton, \(C_{H^+}\), and copper ions, \(C_{Cu^{2+}}\), were adjusted to maintain a constant total concentration at 0.4 M. Both the dipping time into the copper electrolyte and subsequent etching time
was 2 min. The results of the penetration length of the reaction front with respect to \([H^+]/[Cu(II)]\) are plotted in Figure 35f. The penetration length dramatically increased when the \([H^+]/[Cu(II)]\) was changed from 0.2 to roughly 0.5, but a further increase in \([H^+]/[Cu(II)]\) resulted in smaller penetration lengths. The large increase is due to the increasing proton concentration that significantly enlarges the porosity, resulting in a faster penetration rate of copper ions. After the penetration length reaches a maximum, the dominate process with increasing reactant concentration ratio, is displacement and the decline in the penetration length of the reaction front is due primarily to the lower copper concentration. Thus, there is a balance between the amount of proton and copper species required.
Figure 35. [H⁺]/[Cu(II)] effect on penetration length. SEM images of Ni-Fe-Co nanowires after dipping into the copper-citrate electrolyte with varied proton and copper ion concentration, with a ratio of (a) 0.2, (b) 0.4, (c) 0.8, (d) 1.6, and (e) 3.2, total reactants concentration 0.4 M, dipping time and etching time 2 min. (f) The summary of the penetration length with [H⁺]/[Cu(II)]. Scale bar 1000 nm.

In order to capture the distance of the reaction front during the propagation of Cu(II) undergoing a displacement reaction and the H⁺ corroding the alloy, a series of experiments were addressed with different dipping times of Fe-Ni-Co nanowires. The penetration length at dipping time of 2 min, 4 min, and 8 min were monitored for the copper solution that had a Cu(II) concentration of 2X(Figure 36 a-c), 1X(Figure 36 d-f), 1/2X(Figure 36 g-i), 1/5X(Figure 36 j-i), respectively. The penetration length of where the reactions occur were measured following etching. These results are summarized in Figure 36m. The linear relationship between penetration length and
dipping time for the 2X, 1X, and 1/2X group indicated a reaction under kinetic control behavior. In contrast, as the [Cu(II)] decreased to 1/5X, the penetration front doesn’t show a linear relationship with time. This could due to the transport limitation of Cu(II) inside the nanopores which results in a diffusion control of the displacement reaction.

![Figure 36](image.png)

**Figure 36.** Varying dipping time induce penetration rate change, the concentration of Cu(II) effect the ion penetration from kinetic control to mass transport control, pH 1.

### 5.3.2 Modeling

During the electrochemical displacement reaction of Fe(s) by copper ions within the nanowires, facilitated by corrosion of Fe(s) by protons, the total current
density is zero and the partial current density of Fe, $i_{Fe}$, is due to both the rate of copper and proton reduction. The corresponding Fe(s) reaction rate, $\frac{i_{Fe}}{nF}$, where $n$ is the number of electrons transferred and $F$ Faraday’s constant, under kinetic control can be represented by Eq 9, assuming first order behavior.

$$\frac{i_{Fe}}{nF} = k'_{Cu} C_{Cu} + k'_H C_H$$  \hspace{1cm} (9)

The rate constants follow a general Tafel model $k'_{Cu} = k_{Cu} \exp \left( \frac{-q_{Cu}FE}{RT} \right)$, $k'_H = k_H \exp \left( \frac{-q_{Fe}FE}{RT} \right)$ for the displacement reaction with copper ions and the dealloying corrosion reaction with protons, respectively. Copper reduction in acid is reported to be first order [149, 150], and proton reduction in acid typically follows a Volmer-Heyrovsky mechanism[151] being first order in proton concentration. In Figures 33-35 the penetration length of the copper propagating into the Fe-Ni-Co wire is clearly not linear with the electrolyte species concentration. However, the active area term is related to the species concentration that creates a non-linear behavior in the penetration length. The penetration rate of the reaction front, $v$, therefore can be described as $\frac{Mw}{\rho \pi r^2} \frac{i_{Fe}}{nF}$ \cdot \text{active area}$, with $Mw$ representing the molecular weight of Fe, and $r$ the radius of the template pore. The difficulty in describing $v$ lies in the
description of the changing active area. As a generalized approach to describe only
the trends of concentration on $v$ the active area was assumed to be some function of
porosity and that this porosity would depend on the ratio, $[H^+]$/[Cu(II)], represented as
$x$. Thus, a power function, $x^p$, times the initial cross sectional area of the pore was
used to represent the active area, where $p$ is a fitted parameter. Combining Eq 9 with
the penetration rate, dividing the penetration rate with the sum of the total reacting
species concentration, $C_H + C_{Cu}$, and rearranging to express $v$ as a function of the
concentration ratio, $x$, gives Eq 10

Assuming that only Fe(s) is principally corroded and displaced, $\frac{M_w}{\rho}$ has a
value of 7.09 $cm^3/mol$ with bulk properties. Figure 36 depicts the scaled results
using all the data presented in Figures 33-35 with fitted constants, using a nonlinear
regression routine (MatLab, R2016b, nlinfit). The values of the fitted constants are:

$k'_H = 0.67 \text{ nm} \cdot L/s \cdot cm^3 \quad k'_{Cu} = 9.8 \text{ nm} \cdot L/s \cdot cm^3$, and $p = 0.23$. The curve
in Figure 36

$$\frac{v}{C_H + C_{Cu}} = \frac{M_w}{\rho} \left[ k'_{Cu} \frac{1}{1+x} + k'_H \frac{x}{1+x} \right] x^p$$

(10)

represents Eq 10 with fitted parameters and captures the trend of the penetration rate
with composition ratio, showing a maximum value when \([H^+]/[\text{Cu(II)}]\), or \(x\), is approximately 0.5. Therefore, the highest displacement rate and penetration of copper into the Fe-rich nanowire alloy occurs when there is roughly 2 times the amount of protons compared with copper ions. This calculation is only an estimate as it does not take into account the type of copper species, and possible diffusion limitations at very low copper ion concentration or very low \(H^+\) concentration.

Figure 37. Scaled penetration rate. Experimental data, circles, compared to a simple fitted kinetic model, curve that describes the anodization of Fe by copper ion reduction and proton reduction, dipping time and etching time 2 min.
The strength of this continuum scale modeling approach is that it can capture of behavior of the penetration region to guide others in solution preparation. However, the disadvantage of this approach is that the details of the structure are not given. The KMC model is an attempt to provide more insight into the structural changes.

5.3.3 Thinning

When using a particular composition for the displacement/dealloying electrolyte there is also flexibility in shaping the etched region by the time of exposure in the etching solution. Figure 37 are TEM micrographs of Fe-Ni-Co nanowires electrodeposited into the template, displaced by copper ion reduction and dealloyed by the proton from an electrolyte containing 0.15 M of copper sulfate at pH 1, followed by etching in the pH 5 boric acid-citrate solution. The Fe-Ni-Co diameter before etching was $109 \pm 4$ nm. As the etching time increases from 1 and 3 min, the diameter of the thinned region decreases nearly proportionally with time, from $79 \pm 2$ nm to $37 \pm 2$ nm, respectively. At 5 min the inner, thinned wire is indeed a little thinner, but not proportionally thinned and starts to detach from the larger segment, indicating that there is a change in the etching process. Etching the copper rich region
did not result in a porous region with the same diameter, but clearly a thinned region.

We suspect the thinning effect has a surface diffusion component that reconstructs a porous structure into a more compact structure, similar to that reported for Au during the displacement of Ag [69, 73, 80].

![Figure 38. Etching time effect on penetration length. (a) TEM image of nanowires after dipping them into a copper-citrate electrolyte, pH 1, copper ion concentration 0.15 M, 2 min. (b-d) TEM images of nanowires after dipping them into a copper-citrate electrolyte, and subsequently etching them in a pH 5 boric acid-citrate electrolyte for 1, 3 and 5 min.](image)

5.4 Kinetic Monte Carlo (KMC) simulation

KMC simulation was applied on a pure, solid copper system, and different displacement/dealloying systems. The influence of remaining Fe, and Ni atomic percentages on the after-thinning nanowire structures were investigated.

5.4.1 KMC simulation of Cu(II) penetrate into Fe-Ni nanowires
Figure 39 shows the KMC simulation of Cu(II) propagation into the Fe-Ni nanowire driven by the reduction reaction of Cu(II) to Cu(s) by the oxidation of Fe(s) to Fe(II) and its redistribution by solid state diffusion. Figure 39a is the Fe(71%)-Ni(29%) alloy before Cu(II) penetration, with simulation size of 20X20X100, that defines the simulation box. Assuming a bcc structure, there are initially 20,000 atoms and an equal number of empty spaces. Figure 39b is the Cu-Fe-Ni porous nanowires after Cu(II) penetration and dealloying with a total KMC simulation steps of 20000. This simulation used following parameters: oscillation frequency for dissolution of 10^65, Fe-Cu bond energy of 0.33 eV, displacement/dealloying probability ratio of 1, and all other parameters are same as mentioned in section 4.

The results indicated that after Cu(II) displacement and dealloying reaction, there is 36.7 wt % of porosity created and 23.7 wt% of Fe and 8.4 wt% of Ni left. In the following results, the initial Cu-Fe-Ni alloy composition will be adjusted by changing the Fe-Cu, Ni-Cu bond (varying from 0.26 eV to 0.40 eV), and the displacement/dealloying probability to simulate the thinning behaviors of nanowires.
with different composition.

![Diagram](image)

**Figure 39.** KMC simulation of Cu(II) propagation into a Fe-Ni nanowire. (a) Fe(71%)-Ni(29) alloy before Cu(II) penetration, (b) Cu-Fe-Ni porous nanowires after Cu(II) penetration and dealloying. Simulation size 20X20X100, total KMC simulation steps = 20000.

### 5.4.2 KMC simulation of nanowire thinning

A pure, solid copper nanowire system is first investigated, the results of the KMC simulation of the thinning process are illustrated in Figure 40, with a total 5000 atoms. As the images show, a pure, solid copper nanowire thinned from the outside...
can keep a uniform diameter in the axial direction only at the initial stage, after the nanowires are etched deeply, it will start to break. This simulation result fits well with the general knowledge that a system has an automatic tendency to keep the overall system surface energy at its lowest value.

![Simulation of pure, solid copper nanowire thinning](image)

Figure 40. KMC simulation of pure, solid copper nanowire thinning, from left to right are the initial copper nanowire, the copper nanowire after being thinned by 400 KMC steps, 800 KMC steps, 1200 KMC steps, and 1600 KMC steps, respectively.

Cu-Fe-Ni nanowires, as evident experimentally, in section 5.3.4, can exhibit a uniform thinning feature in a pH 5 etchant, where Cu was able to dissolve but Fe and Ni atoms are largely protected by passivation. A particular interest of this research is
to understand the influence of the remaining Fe, and Ni atoms percentage on the final thinned structure. Figure 41 is the KMC simulation of a porous copper nanowire thinned with an initial Cu-Fe-Ni nanowire containing 10.0 wt% of iron group atoms \((\text{Fe} + \text{Ni})\) (a), 17.1 wt% of iron group atoms \((\text{Fe} + \text{Ni})\) (b), 22.8 wt% of iron group atoms \((\text{Fe} + \text{Ni})\) (c), and 30.8 wt% of iron group atoms \((\text{Fe} + \text{Ni})\) (d), respectively. For each simulation group, from left to right are the initial copper alloy nanowires containing, a copper nanowire after thinned by 0 KMC step, 400 KMC steps, 1200 KMC steps, 2000 KMC steps, respectively, representing a progression in time. The expanded view image in the boxed area is used for exhibiting more detail. Based on the thinned structure of the nanowire after 2000 steps, there is a clear trend that Cu-Fe-Ni was hard to keep in an unbroken structure when there is only 8.9 wt% of iron group atoms left in the initial nanowires, but as the percentage of Fe and Ni atoms increase to 16.9 wt% and higher, the nanowires show a uniformly thinning feature. The local images of the after-thinned nanowires (in box) illustrate that Fe and Ni atom can act as an anchor to capture the neighboring Cu atoms from being removed. When there is enough Fe and Ni atoms locally, the Cu-Fe-Ni nanowire can
avoid breaking during the thinning process. Meantime, the “jump” of Fe and Ni atoms through surface diffusion facilities the nanowires to retain a relatively smooth surface during thinning. It’s important to emphasize that too much Fe and Ni atoms trapped in the initial Cu-Fe-Ni nanowires can have negative effect for the thinning process due to the “frame-effect”, where Fe and Ni hold the original shape and size of the nanowire leads a more porous structure instead of a thinned nanowire.
Figure 41. KMC simulation of porous copper nanowire thinning. Initial Cu-Fe-Ni nanowires containing 10.0 wt % of Fe and Ni atoms (a), 17.1 wt % of Fe and Ni atoms (b), 22.8 wt % of Fe and Ni atoms (c), and 30.8 wt % of Fe and Ni atoms (d), are thinned and tracked. For each group of simulation, from left to right are initial copper nanowire containing, copper nanowire after thinned by 400 KMC steps, 1200 KMC steps, 2000 KMC steps, respectively. The image highlighted in the box is a local zoom in result to show more detail.

5.5 Cu-Mo-Iron group alloy nanowire fabrication

Fig. 42 presents SEM images and composition data of the nanowires before and after they have been exposed to the copper-citrate electrolyte. Prior to dipping the Fe-Ni-Co embedded wires into the copper-citrate solution, the nanowires were first characterized. Fig. 42a shows released Ni-Fe-Mo nanowires electrodeposited for 5000 s. The wire lengths were roughly 8 microns, reaching the end of the template. The average deposit composition of the array of the wires before they were released was $57 \pm 1.7$ wt % Fe, $18 \pm 1.1$ wt % Ni and $26 \pm 2.3$ wt % Mo, with the current efficiency of approximately 10 %. To the best of the authors’ knowledge this is the first demonstration of an Fe-Ni-Mo electrodeposited nanowire.

Several Fe-Ni-Co alloy nanowire arrays were electrodeposited under the same conditions and then exposed to the copper-citrate solution at different lengths of time.
The resulting average composition change (Fig. 42b) was measured, which reflects the propagation of the Cu(II) displacement reaction. It is expected that this reaction is not self-limiting to the Fe-Ni-Mo nanowire surface because the low solution pH of the copper-citrate electrolyte was chosen to promote corrosion, thus allowing a pathway for the copper ions to penetrate in the axial direction into the wire when they are embedded in the template. The composition in Fig. 42b is an average one, over a large, 100 micron spot size, analyzing from top to bottom of a collection of nanowires. As the dipping time increases from 0 s to 120 s, there is an increase of the amount of copper in the deposit up to 69 ± 12 wt % Cu at 120 s, which validates the displacement/dealloying concept, and shows that copper was successfully introduced into the Fe-Ni-Mo nanowires. The largest elemental change of the original alloy composition was Fe, as expected, decreasing from its initial composition of 57 ± 2 wt % to 13 ± 7 wt % at 120 s. However, the amount of Ni and Mo also decreased, with the composition falling to 3 ± 1 wt % (-83 %) and 15 ± 4 wt % (-73 %), respectively for a long dipping time of 120 s. Since these XRF composition measurements are average values over a large scale, the exact Cu(II) penetration depth is not possible to
ascertain. Therefore, local compositional information was examined with EDS/SEM.

Fig. 42c, and d shows a collection of bi-layered Cu-Mo-iron group/Fe-Ni-Mo nanowires formed by dipping the pulse electrodeposited Fe-Ni-Mo segments into a pH of 1 copper-citrate solution for 120 s, and released from the template. Fig. 42c is the SEM image where two regions were identified for select area EDS composition analysis, and Fig. 42d shows a Cu EDS mapping. There is a clear change in contrast at the tips of the nanowires. A Cu rich region was verified at the end of the nanowire. This region had a length of 934 ± 31 nm and indicated the depth that the Cu(II) penetrated into the nanowire, thus providing an estimate of the rate of penetration of the Cu(II) into the nanowire, 8 nm/s, selected area composition analysis (Fig. 42c, Area 1) shows that this end region of the wire is indeed copper rich, and in the neighboring region, further down the wire, the local composition has no Cu signal (Fig. 42c, Area 2). In this region, several wires are in a parallel orientation, and this local, average composition of the Fe-Ni-Mo nanowires is 29 wt% of Mo, 37 wt% of Fe, and 34 wt% of Ni. This composition differs from the original, average overall composition (Fig. 42b), having considerably more Fe when the wires were not dipped.
into the copper-citrate electrolyte. At this local position, (Fig. 42c, Area 2), the significantly lower Fe content can indicate that the corrosion reaction from H\(^+\) extended further into the wire than the Cu(II) and/or there is a gradient of composition in the original wire. Nevertheless, the Cu rich region is confirmed, with the nanowire tip has a composition of 14 wt % of Mo, 16 wt % of Fe, 15 wt % of Ni, and 55 wt % Cu. The EDS mapping analysis is also provided for Cu(s) at low magnification. At the edge of the nanowire, the copper signal is apparent, and uniformly distributed in this region.
Figure 42. (a) Low magnification SEM of a collection of Fe-Ni-Mo nanowires with an average composition of 57 wt % Fe, 18 wt % Ni and 26 wt % Mo, (b) Deposit composition after the array of Fe-Ni-Co nanowires were dipped into the pH 1, copper-citrate solution, (c) SEM image and select area EDS composition analysis for a collection of bi-layered Cu-Mo-iron group/Fe-Ni-Mo nanowires formed in a pH 1, copper-citrate solution for 120 s, (d) EDS mapping analysis for Cu.

The structural change of the alloy upon exposure to the copper-citrate electrolyte was examined with TEM-SAED, at the nanowire tip and at a region of the nanowire where Cu(II) had not reached (Fig. 43). The representative bi-layered nanowires were released from their templates and were fabricated with the same conditions as nanowires illustrate in Fig. 42c. In Fig. 43, a low-resolution image
shows that the tip region of the wires, where the Cu displacement occurs, has a lighter contrast than the middle part of the wires, where the Fe-Ni-Mo nanowires are unreacted. Fig. 43b, and c and Fig. 43d, and are TEM-SAED results of the Fe-Ni-Mo region and Cu-Mo-iron group region, respectively. In Fig. 43c, the crystalline structure of electrodeposited Fe-Ni-Mo nanowires has a combination of rings and spots, indicative of a polynanocrystalline structure, the SAED results of the Cu-Mo-iron group alloy depicted in Fig. 43e, shows more diffuse rings suggesting a more amorphous character. At the end of the nanowire the SAED shows Cu (200), Cu (111) and Cu (110) reflections, together with the Fe-Ni-Mo. The size of the rings and dot positions from the center spot in the SAED from the middle region of the nanowire for Fe-Ni-Mo (Fig. 43c), are the same as those at the nanowire tip (Fig. 43e), superimposed with Cu, thus, there is no substantial change in the Fe-Ni-Mo interplanar distance, and the resulting alloy at the nanowire tip is essentially a two-phase material. Phase changes would be expected with a subsequent annealing step, although this was not part of the present study.
Figure 43. HRTEM (a) low resolution images of bi-layered nanowires fabricated by dipping Fe-Ni-Mo nanowires in pH 1 copper solution for 120 s, (b) high resolution image of the middle region of the nanowire and the corresponding (c) SAED of the middle region; (d) high resolution image of the tip region and the corresponding (e) SAED for the tip. Scale bar for (b) and (d) are 100 nm [152].

5.6 Gold coated nanowire and alignment

As one of the most prevalent material used in the biosensor field, gold has extraordinary electronic conductivity, thermal stability, and mechanical ductility. Table 1 shows that the Au\(^{+}\)/Au equilibrium standard potential is much higher than Fe\(^{2+}\)/Fe, Ni\(^{2+}\)/Ni, Co\(^{2+}\)/Co, and Cu\(^{2+}\)/Cu, therefore, the Au element can be electrolessly deposited onto the as synthesized Cu-Fe-Ni-Co nanowires.

Figure 44 shows the HRTEM and SEAD results of the gold coated Cu-Fe-Ni-Co nanowires. The SEAD pattern shows in Figure 44b, which examines the
thinned region (Figure 44a), shows a combination of Au (yellow) and Ni-alloy (white) crystal structure dots, which confirms that the gold was successful deposited.

Figure 45 shows SEM-EDS mapping results for Cu-Fe-Ni-Co nanowires with the thinned region after dipping in a commercial gold solution for 10 min. Figure 45b-f are Au, Cu, Fe, Ni, and Co elements distribution in nanowires depicted in Figure 45a. The result shows in Figure 45b proved that the Au element was uniformly deposited onto the nanowires as illustrated by the appearances of Au signal along the whole nanowire. The signal for Cu was relatively low inducing an obstacle for confirming a predominant region (Figure 45c), which was because of the copper rich region (thinning region) was replaced by gold element. In contrast, Fe (Figure 45d) and Ni (Figure 45e) elements show an obvious weak signal region along the thinned nanowire region, which was due to the displacement reaction of copper in the former steps. Co elements has weak signal along the whole nanowire due to the relatively low percentage (Figure 45f), thus it is not clear if it is a core-shell configuration or if the gold penetrated into the wire leaving some Fe and Ni.
Figure 44. (a) HRTEM images of the Fe-Ni-Co nanowires with the thinned region after dipping in gold solution for 10 min. (b) the SAED pattern of the thinned region. The white label represents Ni, the yellow labels represents gold.

Figure 45. SEM image of Fe-Ni-Co nanowires with thinned region after coated with gold (a), and EDS-mapping of elements, (b) Au, (c) Cu, (d) Fe, (e) Ni, and (f) Co.
Figure 46 shows magnetic alignment capability for Fe-Ni-Co nanowires. First, an Fe-Ni-Co thin film with a thickness of approximately 15 µm was deposited on one side of the Cu plate, then the copper plate was sealed into an epoxy resin substrate but expose on edge by polishing (Figure 46a). The Fe-Ni-Co nanowires was dripped on the copper plate site with and without extra magnetic field. Results in Figure 46a and b clearly show that without extra magnetic field, the Fe-Ni-Co nanowires were dispersed randomly, which proves the magnetic force by the Fe-Ni-Co thin film alone couldn’t align the Fe-Ni-Co nanowires. However, when there is extra magnetic field applied, the Fe-Ni-Co thin film at one side of the copper plate can acting as an anchor to hold the Fe-Ni-Co allows the external magnetic field aligns the Fe-Ni-Co nanowires. Applying the same idea but substituting the epoxy substrate with a nanofluidic patterned substrate (provided by Professor Sunggook Park’s group, Department of Mechanical Engineering at Louisiana State University), the nanowires were successfully aligned cross the nanochannels (Figure 47).
Figure 46. Comparison of Fe-Ni-Co nanowires alignment via magnetic thin film combined without extra magnetic field (a) and with an extra magnetic field (b).

Figure 47. (a) schematic of the proposed nano-sensor platform for biomolecular detection, (b) Fe-Ni-Co nanowires aligned on top of nanofluidic channels.
6 CONCLUSION

The goal of this project is to fabricate nanowires and nanogapped wires with a controllable gap size of 1 - 10 nm as sensors for DNA molecule sequencing. The Super-Invar Fe-Ni-Co alloy was selected as the nanowire material since it is magnetic and can easily be magnetically aligned for easy placement in a device. Guided by RCE experiments, conditions to deposit the Fe-Ni-Co nanowires were determined. Template electrodeposition was used for creating nanowires with a diameter around 100 nm, which were also used for nanogap fabrication.

In the first study, a novel approach for fabricating Fe-Ni-Co nanotips at an interfacial region within the nanowires was introduced via a combination of two steps of pulse electrodeposition separated by an anodic potential. The conditions for the wire layers and the interpretation of their formation was facilitated from the results of thin film electrodeposition and the polarization curves in the deposition electrolyte and in an etching solution. Through tracking the potential transients during nanowire growth, and the current transients during the generation of an oxide layer, the governing chemical environment and reactions were determined in generating
nanowires with a middle layer having a different crystallinity and porosity. When the nanowires are etched, a nanotip forms in this interfacial section when the intermediate oxide deposition potential has a high overpotential, otherwise, it is a nano-gap.

In the region of the nanowires where the metal ions are reduced the structure was amorphous, but in the region where an oxide was formed and then subsequently reduced, the structure was more crystalline, and contributed, in part, to the subsequent tip formation. The reduction of an oxide resulting from the applied potential in step two together with re-deposition of the alloy creates a gradient of porosity, which was suggested to account for the etching of the nanowire in the radial direction of the crystalline region to form the tip.

In the second study, a novel methodology is presented to deposit and thin Fe-Ni-Co nanowires. The proton and copper concentration ratio, [H+]/[Cu(II)], and total moles of reactants during the dipping step, is key to drive the displacement reaction of Fe by copper ion reduction into the Fe-rich nanowire axially in order to create a Cu-rich region to be selectively etched forming thinner segments. The reaction front propagation can be limited if there is not enough proton to etch the
nanowire and it can also be limited if there is not enough copper ions to drive the displacement reaction. A thinned nanowire region connected to a single larger region was demonstrated, as well as a thinned region between two larger regions in a barbell configuration.

A KMC simulation was developed to study both the Cu(II) ion penetration process and the subsequent thinning stage. The model demonstrates that it is possible for Cu(II) ions to penetrate continually into an Fe-Ni alloy utilizing the pores created by proton corrosion, leading to a porous Cu-Fe-Ni nanowire. During the thinning process, Fe and Ni atoms are acting as anchors to capture neighboring copper atoms from being removed, thereby playing a crucial role for achieving a uniform thinning feature. An optimized percentage range, 16.9 wt% - 31.6 wt%, for trapped Fe and Ni atoms at the beginning of thinning is predicted to induced a uniformly thinned nanowire. If there is not enough Fe and Ni atoms in the initial Cu-Fe-Ni nanowire, the etching procedure will lead to multiple breakage points during etching, while too much Fe and Ni atoms will lead a porous structure instead of a thinned structure.

Additionally, Cu rich Cu-Mo-iron group nanowire segments with ~14 wt% of
Mo were successfully fabricated through a combined dealloying/displacement reaction onto and into Mo-Fe-Ni nanowires. This is the first time to the authors’ knowledge that Cu-Mo-iron group nanowires were fabricated through an electrodeposition method. Precursor Fe-Ni-Mo nanowires with approximately 29 wt% of Mo were achieved via template-assisted pulse electrodeposition. Copper ions penetrated the precursor nanowire in the axial direction aided by the corrosion of the nanowire alloy by protons; and copper deposited, in-situ, forming a new Cu-Mo-iron group nanowire segment. SEM and EDS mapping results indicate that the propagation front was uniform, with a penetration rate of roughly 8 nm/s. TEM-SAED analysis suggests that before the nanowires were exposed to the copper-citrate electrolyte, Fe-Ni-Mo had a polynanocrystalline structure. However, after exposure to the copper-citrate electrolyte, the Cu rich region had a two-phase structure, and the Fe-Ni-Mo region became more amorphous.

The results of this dissertation have been published in Nano Letters, and the Journal of Electrochemical Society.
7 RECOMMENDATIONS

1) A very interesting, novel thinning through etching methodology is reported in this research, and the phenomenon is experimentally evidence with the Fe-Ni-Co alloy system with Cu(II) as the propagating ion, and verified with KMC modeling. Future work needs to address the possibility of expanding this methodology into other alloy systems to achieve more potential applications.

2) Making two pairs of parallel arranged nanotips is one target for this project that was not realized, only one tip point near a nano-gap was achieved. Future work would be to develop multiple layers and an altered methodology to create the opposing nanowire tips.

3) Performance of a nanosensors with extremely high requirements of sensitivity is expected to be achieved with a core-shell structure of gold coated Cu-Fe-Ni-Co nanowire. Through this work, gold has been successfully coated onto the Cu-Fe-Ni-Co nanowires, it is not known how far the gold has penetrated into the alloy and future work in this direction would be fruitful.

4) The KMC simulation in this work are restricted by the calculation power of the
computer and the algorithm, and can model an 8nm×8nm×30nm alloy system, which is still far from the real case of 100nm×100nm×2000nm nanowires system. Advanced algorithm, e.g. clustering, k-th nearest neighbor (KNN) in the k-d tree, and accelerated KMC simulation need to develop to expanding the simulation to large scale. Also, the simulation here assumes a bcc structure of Fe-Ni. Electrodeposited Fe-Ni alloys have different structures depending in their composition, including a bcc structure for alloys rich in Fe. Although, the results are not expected to change greatly for a change in the structure, more accuracy could be predicted if a better structural representation of the alloy was provided.
## 8 NOMENCLATURE

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Greek

$\rho$  Density, $g/cm^3$

$\epsilon$  Current efficient

$\delta$  Thickness, $\mu m$

$\nu$  Oscillation frequency, Hz

$\nu$  Penetration rate, nm/s

$\nu$  kinematic viscosity, cm$^2$ s$^{-1}$
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