Electroplated micro- and nanoscale structures for emitters and sensors

2014

Xiaochen Wang

University of Central Florida
ELECTROPLATED MICRO- AND NANOSCALE STRUCTURES FOR EMITTERS AND SENSORS

by

XIAOCHEN WANG
B.S. Shanghai Jiao Tong University 2012

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Materials Science and Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Spring Term
2014

Major Professor: Hyoung Jin Cho
©2014 Xiaochen Wang
ABSTRACT

In the electroplating process, dissolved metal cations are reduced by electrical current to form a coherent metal coating on an electrode. Therefore, electroplating is primarily applied to modify the surface properties of an object (e.g. abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities, etc.), but also be applied to build up high aspect ratio structures on undersized parts or to form devices by electroforming.

Compared with other common MEMS (microelectromechanical systems) metal device fabrication techniques, such as vapor depositions, electroplating has several outstanding advantages. First, the fabrication process is cost-efficient because electroplating process can be set up easily without complex and expensive facilities. Second, the fabrication condition of electroplating is less demanding and does not require high temperature or low pressure. Furthermore, the process is applicable to making various features consisting of nanometer to millimeter scale particles, wires, and films. Thus, in this thesis, based on the design requirements of electrospray emitters and environmental sensors, the electroplating method was chosen to fabricate micro- and nanoscale structures for such applications.

Electrospray is an atomization technique by which an electrically conductive liquid through a small capillary is charged with high voltage (kV) and ejected to a ground electrode. To minimize the electric field edge effect of the emitter nozzles to get even electro-hydrodynamic pulling force on the liquid among the nozzles and minimize variation from one emitter to another, the device needs to have the viscous pressure drop across each nozzle dominant over the electro-
hydrodynamic pulling force. Therefore, embedded structures that can create high flow impedance are desirable to achieve uniform feeding of low flow rate of liquid to each emitter.

We designed and fabricated in-plane metallic electrospray devices with an embedded array of micropillars within a microchannel by photolithography and electroplating. The novelty of the proposed research lies in its embedded flow restriction structure, scalability, and ease of fabrication. The formation of jets as well as the flexing capability of the emitter was achieved.

The other application of electroplating was demonstrated in the fabrication of environmental sensors. Utilizing a pulsed electroplating method, Co-Cu metal alloy films were prepared and Cu was selectively etched to fabricate nanoporous electrodes which could be used to measure both absolute levels and changes of phosphate concentration in aqueous environments. The formation of cobalt phosphate compound could be used for the detection. The increased surface area and relatively simple fabrication protocols make the proposed method attractive and promising for many environmental sensing applications.
ACKNOWLEDGMENTS

At the start of the thesis, the one I mostly want to express my gratitude is my advisor, Dr. Hyoung Jin Cho. During the past months of research, Dr. Cho gave me support, guidance and encouragement. I am not only impressed by his knowledge and ability in science research, but also by his rigorous academic attitude. As a student just joined in research, I met many difficulties and made many mistakes. Dr. Cho guided and helped me to solve problems very patiently rather than blaming me. This gives me confidence to continue after failure and I really appreciate. Besides my ability in doing experiments, Dr. Cho also trained me in different aspects. My speaking and writing are greatly improved and I perform better in presentations. As Dr. Cho said that he would require me as a real PhD student, I will work hard toward this goal.

I would like to thank my other committee members. I am grateful for they can attend my defense to give me guidance to improve my thesis and future work.

I would also like to thank Dr. Weiwei Deng, Dr. Woo Hyoung Lee and their student Dr. Cheng Li, Weiwei Yang and Xiangmeng Ma for their guidance and help for the fabrication and test. They helped a lot in simulation and device test part, which gave me a clear guidance to improve my fabrication. Through cooperating with them, I learn a lot in devices’ working principle, and application that enriched my knowledge.

Finally, I would like to thank my friends in our group and my parents. They encouraged me when I felt depressed during my research. I also appreciate that other members in our group taught me a lot through sharing their research experience with me.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF ACRONYMS (or) ABBREVIATION</td>
<td>xi</td>
</tr>
<tr>
<td>CHAPTER ONE: INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER TWO: ELECTROPLATING TECHNOLOGY</td>
<td>7</td>
</tr>
<tr>
<td>2.1 Electroplating Setup</td>
<td>7</td>
</tr>
<tr>
<td>2.2 Electroplating Parameters</td>
<td>8</td>
</tr>
<tr>
<td>2.3 Properties of Electroplating Device</td>
<td>12</td>
</tr>
<tr>
<td>CHAPTER THREE: HIGH ASPECT RATIO EMBEDDED PILLAR STRUCTURE FOR MULTIPLE EMITTERS</td>
<td>15</td>
</tr>
<tr>
<td>3.1 Design Requirements</td>
<td>15</td>
</tr>
<tr>
<td>3.2 Simulation</td>
<td>18</td>
</tr>
<tr>
<td>3.3 Fabrication</td>
<td>22</td>
</tr>
<tr>
<td>3.4 Test</td>
<td>26</td>
</tr>
<tr>
<td>3.5 Results and Discussion</td>
<td>29</td>
</tr>
<tr>
<td>CHAPTER FOUR: NANO STRUCTURED METAL FILMS FOR PHOSPHATE SENSORS</td>
<td>38</td>
</tr>
<tr>
<td>4.1 Design Requirements</td>
<td>38</td>
</tr>
<tr>
<td>4.2 Fabrication</td>
<td>40</td>
</tr>
<tr>
<td>4.3 Test</td>
<td>43</td>
</tr>
</tbody>
</table>
4.4 Results and Discussion .............................................................................................................. 45

CHAPTER FIVE: CONCLUSION AND FUTURE WORK ................................................................ 51

5.1 Conclusion ................................................................................................................................. 51

5.2 Future Work ............................................................................................................................... 52

APPENDIX A: ELECTROPLATING OF EMITTER ....................................................................... 53

APPENDIX B: ELECTROPLATING OF PHOSPHATE SENSOR ......................................................... 56

LIST OF REFERENCE ..................................................................................................................... 59
LIST OF FIGURES

Figure 1 Electroplating setup: (a) schematic view (b) actual view ................................................................. 7
Figure 2 Schematic representation of Nernst layer ....................................................................................... 10
Figure 3 Current mode. (a) Single direction pulse current and (b) pulse current with reversed current .................................................................................................................................. 11
Figure 4 Smoothing effect due to the dissolution of metal while the current is reversed ......................... 12
Figure 5 Emitter with artificial porous media structure[25] ....................................................................... 17
Figure 6 Emitter nozzle with high aspect ratio micro pillars ..................................................................... 18
Figure 7 Photomask design and design parameters ..................................................................................... 19
Figure 8 Simulation result of pressure field in the nozzle (in Pa) ............................................................... 20
Figure 9 Flow velocity distribution (in m/s) .................................................................................................. 21
Figure 10 Bottom layer fabrication. (a) Au/Ti seed layer deposition, (b) photoresist patterning, (c) Ni electroplating and (d) photoresist stripping ...................................................................................... 23
Figure 11 Alignment procedure for pillar and side wall structures ............................................................. 24
Figure 12 Fabrication process of inner structure and top layer. (a) Fabricated bottom layer, (b) photoresist patterning, (c)-(f) Ni electroplating and (g) photoresist stripping and device releasing. .......................................................................................................................... 25
Figure 13 Fabricated device ........................................................................................................................ 26
Figure 14 Measurement of surface profile .................................................................................................. 27
Figure 15 Functional test set up: (a) schematic view and (b) actual view ................................................. 28
Figure 16 Thickness of electroplated structure as a function of time ....................................................... 29
Figure 17 Optical observation of bottom layer fabrication: (a) after PR patterning, (b) after striking treatment and (c) after electroplating.

Figure 18 Top layer and cap formation: (a) patterned PR, (b) formation of micropillars, (c) formation of mushroomed cap layer (d) enclosed device.

Figure 19 Defective pattern formation. (a), (b) underdeveloping and (c) overdeveloping.

Figure 20 Defective patterns resulted from underdeveloping.

Figure 21 SEM pictures of (a) layer after Ni striking, (b) bottom layer, (c) micropillars and side walls near the nozzle tip, and (d) micropillars in the middle.

Figure 22 Inner structure of fabricated emitter. (a) Broken nozzle, (b) and (c) side view of a fractured nozzle portion.

Figure 23 Formation of a air bubble at the tip which verifies the clear passage within an emitter.

Figure 24 Formation of a jet at the emitter tip.

Figure 25 Multi-directional jetting. (a)-(f) the emitter jets continuously and consistently with different flexing angles from 0° to 26°.

Figure 26 Co-Cu alloy phase diagram[30].

Figure 27 Sensor electrode layer fabrication process: (a) Au/Ti seed layer deposition, (b) photoresist patterning, (c) Co-Cu alloy electroplating, (d) photoresist stripping, and (e) selective etching of Cu to form a nanoporous electrode layer.

Figure 28 Schematic view of a sensor device. (a) Fabricated chip and (b) packaged device.

Figure 29 Experiment setup. (a) schematic view and (b) actual view.
Figure 31 AFM results of electrode fabricated with different current density: (a) 75mA/cm$^2$, (b) 120mA/cm$^2$ and (c) 150mA/cm$^2$.

Figure 32 EDS measurement. (a) 5s etching and (b) 10s etching.

Figure 33 Sensor electrodes surface morphology SEM pictures. (a) Co-Cu alloy before etching, and (b) after etching.

Figure 34 Sensor electrode test results. (■: Planar Co electrode; ●: Nanoporous electrode)
# LIST OF ACRONYMS (or) ABBREVIATION

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BOE</td>
<td>Buffered Oxidation Etch</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DI water</td>
<td>Deionized water</td>
</tr>
<tr>
<td>kV</td>
<td>KiloVolt</td>
</tr>
<tr>
<td>MEMS</td>
<td>Micro-Electro-Mechanical Systems</td>
</tr>
<tr>
<td>PCB</td>
<td>Printed Circuit Board</td>
</tr>
<tr>
<td>PEB</td>
<td>Post Exposure Bake</td>
</tr>
<tr>
<td>PEP</td>
<td>Pulsed Electroplating</td>
</tr>
<tr>
<td>PR</td>
<td>Photoresist</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions Per Minute</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
</tbody>
</table>
CHAPTER ONE: INTRODUCTION

Microelectromechanical systems (MEMS) are increasingly used in sensor and actuator applications. Many MEMS fabrication techniques were well-established. Among those, one of the widely used methods is electroplating process. Although the electroplating method has been used mainly for surface modification traditionally, nowadays it is combined with photolithography for making high aspect ratio structural or sensing components in MEMS. Micro switches[1], relays[2], valves[3], pumps[4], heaters[5] and gyroscopes[6] have been realized by patterned layers of different metals and alloys such as nickel, nickel alloys, gold alloys, silver and copper. For high performance components, the metal layers have to meet the requirements on chemical homogeneity, as well as mechanical, electrical or magnetic characteristics. The application of microelectroplating has to deal with specific effects influencing the electroplating conditions at the reduced scale ranging from a few nanometers to hundreds of micrometers. Therefore, many efforts have been concentrated on the control and standardization of microelectroplating processes[7].

Electroplating is a relatively simple process that can be done in an electrolyte solution with inexpensive equipment. The process is analogous to a galvanic cell acting in reverse. Electroplating process for MEMS devices are often performed on a silicon wafer as a plating substrate. Starting with a high quality metallic seed layer deposited by e-beam or thermal evaporation, a photoresist (PR) is spin-coated and patterned by photolithography. The patterned opening is used as a plating mold. This resist pattern as well as plating conditions influences the growth uniformity, morphology and composition of the layer. Thus, these conditions need to be
optimized for successful MEMS device applications[8]. Various electroplating modes are used depending on specific requirements. Design and operating parameters of the electroplating bath such as current mode and density, electrode, electroplating bath and plating temperature primarily decide the uniformity, grain size, residual stress, morphology and composition of the deposited layer in general.

Usually, the object to be plated works as a cathode and is maintained at a negative potential. For an anode, there are various choices of materials[9]. In some cases, a soluble anode is made of the same metal to be plated on cathode. Both components are immersed in the electrolyte solution containing one or more dissolved metal salts as well as other ions for buffering and tuning the electrolyte solution’s conductivity. In other cases, noble, insoluble metals are used as an anode. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, vis-a-vis the current flowing through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode[9].

Different from the first technique, another kind of electroplating processes uses non-consumable anode such as platinum or carbon. In these techniques, ions of the metal to be plated must be periodically replenished in the bath as they are depleted in the solution. This may be more economical when the metal salts are much cheaper than the metal itself.

The uniformity of the plating thickness and morphology across the wafer are increased by including surfactants, which improves the wetting property. In order to supply current to the
anode, oxidize the metal atoms that comprise it and allowing them to dissolve in the solution, a power source is essential.

Besides the differences in electrodes, the fabrication results also depend on the current mode. Typically, direct current (DC) electroplating is the basic method that a DC power supply is used (potentiostatic) and the voltage is adjusted to obtain the desired current density. During plating, the impedances of the electrodes is changing, so an alternative approach that tune the current (amperostatic) is applied to maintain a more constant current density. Based on DC electroplating, there is an improvement to pulse the current on and off at a specified duty cycle, referred to as pulsed electroplating (PEP)[10]. In PEP, higher peak currents than for DC plating is necessary to obtain a comparable plating rate. By reducing into metal atoms, cations in the region closest to the cathode is depleted during each plating pulse, therefore one benefit of PEP is that diffusion of cations species from the bulk solution in between current pulses can recharge the region so that the plating process is uniform. This can raise the reactant concentration at the interface, which otherwise is depleted during DC plating.

PEP has several advantages: 1) DC current favors the growth of existing metal grains leading to a larger grain size, while pulse current favors the nucleation of new grains resulting in much finer-grained metal deposits; 2) morphology and stress control is facilitated by adjusting the duty cycle; 3) control of crystal orientation through PEP can improve electrical and wear properties of plated films; and 4) PEP allows the electroplating process to provide better deposition in corners or spaces[11].
MEMS devices have certain requirements in precision features, material microstructure, morphology and uniformity. PEP works well on these aspects both for thick and thin layer devices.

One of the applications of PEP in this thesis is fabrication of high aspect ratio structure for electrospray emitters. Electrospray is an atomization technique by which an electrically conductive liquid through a small capillary is charged with high voltage (kV) and ejected to a ground electrode. The size of droplets is dependent on multiple parameters including the liquid conductivity, flow rate, and evaporation rate of the liquid [12]. Although electrospray has been studied widely, especially for its application in mass spectroscopy, it gained a renewed attention due to its scalability and direct-writing capability on various substrates, which promises cost-effective nanomanufacturing. Another interesting application area of the electrospray is space propulsion which takes advantage of the high specific impulse produced by electrospray operated in the ionic regime. In both cases, in order to scale up the throughput or increase the thrust power, utilization of multiple electrospray emitters is considered as a viable approach. However, even with identical nozzles, the electric field near each nozzle may not be identical due to edge effects. This non-uniformity leads to an uneven electro-hydrodynamic pulling force on the liquid among the nozzles, yielding different flow rates from one emitter to another. The solution is to make the viscous pressure drop across each nozzle dominant over the electro-hydrodynamic pulling force. Therefore, embedded structures that can create high flow impedance are desirable to achieve uniform feeding of low flow rate of liquid to each emitter.

In this thesis, photolithography and PEP fabrication techniques were combined to address these known challenges. Using a batch fabrication method, multiple identical electrospray units for
testing were made concurrently with high precision without resorting to the traditional machining techniques. At the same time, in-plane high flow resistance structures could be fabricated. We embedded an array of micropillars within a microchannel for such purpose[13]. The novelty of the thesis topic lies in its embedded flow restriction structure, scalability, and ease of fabrication. Test results shows that these in-plane structures increase the effective channel length and thus, flow impedance. In addition, the in-plane design allows us to integrate more sophisticated microfluidic features that further increase the flow impedance while preventing clogging.

In an effort to fabricate this emitter, several PEP parameters are studied and optimized through experiments. According to our design, an array of micropillars could be concurrently fabricated within the emitter channel. The individual diameter of the micropillar was around 30 μm and the gap between the micropillars was 10 μm.

Different from emitters, for sensor applications, surface characteristics are more important. Therefore, a thin layer of alloy (1-3 μm or less) film is the subject of study. In such case, the focus of investigation is more on the morphology, composition and nanostructure of the thin film, where the electrolyte constituents, PEP current density and duty cycle play important roles. More specifically, the objective of the second part of thesis study was the development of an environmental microsensor that can measure both absolute levels and changes in chemical species in the aqueous environments[14]. Among these applications, measurement of phosphate is the main interest of this study. Phosphate is an essential nutrient for plants, and its measurement has been useful to control the amount of fertilizers applied to maximize crop yield from hydroponics in agriculture, or monitor undesired growth of algae and other aquatic
vegetation to prevent the eutrophication of natural water bodies[15]. Due to the above reason, there has been accelerating progress in the development of simple and compact phosphate sensors.

Cobalt-coated needle-type microelectrode array sensor for measurements of phosphate was reported before based on MEMS technologies, which was tested with potassium sulfate solution in the concentration range of $1 \times 10^{-5.1} - 1 \times 10^{-3}$ M at pH 7.5. The repeatable phosphate-selective potentials with a sensitivity of $\sim 96$ mV per decade were exhibited with less than 30s response times and good signal stability[16].

However, the fabrication protocol for this sensor requires etching and assembling steps. In our approach, a planar cobalt microelectrode with a high surface area was fabricated through PEP. A key idea is to use special nanostructures such as nanowires and nanopores to enhance the surface area that could be used as an electroactive site. For this, cobalt-copper alloy PEP and dealloying (selective etching)[17] process followed by oxidation was utilized to attain nanoporous cobalt oxide structures for a phosphate sensor electrode.
CHAPTER TWO: ELECTROPLATING TECHNOLOGY

Traditionally, electroplating is the process of depositing a coating with a desirable form by means of electrolysis, which is carried out in a solution (“bath”) may consist of fused salts or of solutions of various kinds. But in commercial and experimental practice it is almost always a water solution. Its purpose is generally to alter the surface characteristics so as to provide improved appearance, ability to withstand corrosive agents, resistance to abrasion, or other desired properties or a combination of them.

Recently, with the development of fabrication technology of MEMS devices, the electroplating technology is widely used for a surface micromachining method with many advantages over other methods such as vapor-based or solution-based deposition techniques.

2.1 Electroplating Setup

Figure 1 Electroplating setup: (a) schematic view (b) actual view.
A common setup for electroplating is shown in Figure 1 with several key components: a cathode and an anode, a current source, a thermometer, a pH meter, a plating vessel, a hot plate and a magnetic stirring bar.

2.2 Electroplating Parameters

Even though the theory and experimental setup could be described as simple, bath constituents, bath temperature and pH, and current mode need to be adjusted to obtain desired structures.

2.2.1 Bath Constituents

In order to avoid the metal ion depleting rapidly from the solution at the cathode surface, concentrated solutions are used. This requires salts with high solubility.

The anion may have profound effects on deposition, even though it does not enter directly into the plating process. When the anion is strongly absorbed on the surface of a cathode, it influences the structure of the deposit strongly. It also affects the activities of the ions. In general, primarily through controlling of the salt solubility related to the concentration, activity and transport number of the metal ion in the bath, and secondarily through salt’s tendency, the effect of the anion is exerted to coordinate with metal ions and cathode surface, influencing the deposition process by adsorption or bridging effects[18].

According to the plating requirement, certain substances (often organic) in small amount, are included in the bath solution to achieve expected form or structure of deposits. Substances adsorbed on the cathode surface during electrolysis have a significant effect on the plating process. Some substances may most often lead to undesirable effects, but when a bright or
leveled surface is produced or internal stress is reduced, the added substance is no longer considered as a contaminant.

Hydrogen bubbles are usually also produced on the cathode simultaneously during the electroplating process. If these bubbles stick to the cathode surface, plating is prevented around the bubble and this results in a pit in the coating. Wetting agents are added to some baths to promote detachment of bubbles and eliminate pitting.

Some salts and acids are also added into the baths to improve the electrical conductive, prevent hydrolysis, function as buffers and increase polarization at the cathode while decreasing it at anode. Thus, for every electroplating process, bath constituents are carefully selected to obtain an optimized fabrication results[18].

2.2.2 Bath Temperature and pH

It was found that, generally, the efficiency of electroplating from ionic solutions is influenced by temperature. While continuing improvements in plating efficiency as the temperature increased is shown in some solutions, most solutions have optimum plating temperature ranges. A certain temperature is necessary to be reached in order to induce the formation of a different metal complex before electroplating was achievable[19].

The pH influences the electroplating process through influencing the hydrogen discharge potential, the precipitation of basic inclusions, the composition of the complex or hydrate from which the metal is deposited, and the extent of adsorption of additive agents. The best pH range is determined empirically because it is not possible to predict these factors theoretically. The effect of pH on stress and hardness is probably exerted mainly through the nature and
distribution of inclusions. In baths containing complex ions, pH may influence equilibria between various complexes present and must be considered in relation to concentrations of metal and cyanide.

2.2.3 Current Mode

There are usually two current modes for electroplating process. One is a traditional DC mode and another mode is a pulse current mode with different sub-modes[20].

The pulse current mode is selected for several advantages. One of the most important features of this mode is the prevention of depletion of cations in the Nernst diffusion layer. In addition, emetal morphology can be adjusted through controlling diffusing process of cations in the Nernst layer. Figure 2 schematically illustrates the Nernst layer.

![Figure 2 Schematic representation of Nernst layer](image)

10
Figure 3 Current mode. (a) Single direction pulse current and (b) pulse current with reversed current.

There are two basic pulse current modes as shown in Figure 3. In case (a), only forward current is output at a given frequency. An important parameter of pulse current, “duty cycle, $\varphi$” is defined as the ratio of $t_{on}$ to $t_{total}$, that $t_{total}=t_{on}+t_{off}$. Usually duty cycle has effect on the composition of electroplated alloys and also morphology. In one cycle, during the $t_{off}$, there is no potential on electrode and also no electrical field between them. Therefore ions do not move under the electrical field any more but diffuse from high to low concentration area, which mitigates depletion. In this way, depletion of cations near cathode is suppressed. Besides suppression of depletion of ions, a short time reversed current (Figure 3, (b)) is often used to gain a smooth surface. As Figure 4 shows, during the electroplating process, the plated surface is usually rough with convex and groove because of non-uniform distribution of electrical fields or ions. This non-uniformity usually has an adverse effect on the performance of electroplated devices. During the plating process, a reversed current will lead to preferential dissolution of protruded metal layers due to the concentrated electric field. Therefore, the convex part will be removed and then lead to a smooth surface.
Figure 4 Smoothing effect due to the dissolution of metal while the current is reversed.

Actually, there are many current modes based on combination of these two modes for achieving different fabrication requirements.

2.3 Properties of Electroplating Device

2.3.1 Mechanical properties

Compared with ceramic materials which have higher hardness but are brittle, metals are used for devices because of good mechanical properties, such as strength and ductility. In general, there are several factors related to the mechanical properties of metallic materials, like grain size, defects, additional agents and co-deposited foreign materials. These factors are directly decided by the electroplating parameters. Thus, fabrication parameters are adjusted so that the fabricated devices’ mechanical properties satisfy design requirements.

Fabricated devices are used in complex environments where stress corrosion and cracking is a mechanism frequently involved in the failure of devices. Tensile strength and ductility of the device are core factors of resisting stress corrosion cracking. During the test the emitter is bent to different direction to a certain degree, thus the strength and ductility of device should be large enough so that the emitter does not fracture.
2.3.2 Residual Stress

Electrodeposits are often laid down in a state of internal or residual stress that all or part of it remains in the deposits. There is one type, macrostress, that behaves through bending a plated metal layer into a curved shape. Macrostress can cause distortion, cracking of the deposits, loss of adhesion to the substrate and, if tensile, poor fatigue property. The other type, microstress, behaves primarily in an increase in hardness. The formation of residual stress may be due to a crystal lattice mismatch between the substrate and deposit, as the deposited atoms try to follow the lattice structure of the surface onto which they are plated. Stresses may also arise from the effect that impurities in the deposit material have on its crystal structure[21]. Residual stress represents an important factor in practical MEMS electroplating. It can cause the plated structure to deform the photoresist pattern, which often results in an end-product that does not follow the desired dimension. Finally, high internal stresses can result in cracking or premature separation of the electroplated devices while plating is still going on. The fabrication conditions like salts species, concentration and distribution and addictive agents greatly affect the magnitude of residual stress.

2.3.3 Adhesion

If the coating lacks adhesion, it will peel off from the substrate because of mechanical forces or deformation, or blowing off by gases, or exfoliating by corrosion. As discussed, there exists a residual stress that deforms the devices during the electroplating process. If the adhesion of devices’ bottom layer to substrate is not strong enough, devices can be detached from the substrate before finishing the fabrication process, which will interrupt fabrication. In order to
obtain a good adhesion, a pretreatment such as ‘striking’ is used to clean the substrate surface and grow a thin layer metal seed layer with good quality and adhesion.

2.3.4 Morphology

For electroplated devices, morphology focuses on the grain shape, texture of the metal layer and surface structure, which are directly related to the mechanical properties and performances of fabricated devices. Morphology can be adjusted by the electroplating parameters such as current density and mode to fulfill the design requirements. For emitters with a thick layer structure which requires good strength and low residual stress, small grains is necessary that can be obtained by electroplating with small current density. For sensor electrodes, the microstructure of the metal layer is the key factor so that a special current density and mode are used to fabricate the nanoporous structure. Morphology can be observed through optical microscope, SEM and AFM to show whether it meets design goals.
CHAPTER THREE: HIGH ASPECT RATIO EMBEDDED PILLAR STRUCTURE FOR MULTIPLE EMITTERS

3.1 Design Requirements

3.1.1 Background

Integrating electrospray into MEMS and microfluidic systems supports application in diverse fields from biotechnology to aerospace. As the key portion of the electrospray setups, emitters play the most important role. Therefore, researchers did a lot of studies on the influencing factors for fabricating electrospray emitters that perform ideally. It is known that the performance of emitters is closely related to species of materials, emitters’ size and shape, and the inner structure of emitter’s nozzle.

3.1.2 Materials

For MEMS devices, material properties have a great effect on the device performance. Several materials have been used for emitter fabrication. The electrospray device works with applying a high voltage between the emitter and a ground electrode. Devices fabricated with silicon are prepared through etching methods, which require high cost fabrication equipment and complex processes[22]. Enclosed nozzle structure is also difficult to obtain with etching method. One needs to consider materials’ strength and robustness for practicality. One of the primary objectives is to produce emitters with a large degree of flexing capability, which restricts the use of silicon. Therefore, metals with robust structure and good corrosion resistance are required in this work. Enclosed metal structure can be achieved by electroplating. Due to its robustness and well-known plating conditions, nickel was selected for emitter[23].
3.1.3 Geometry

Compared to macroscopic devices, MEMS devices have smaller form factors ranging from micron to millimeter scale, where the geometry of devices have a much greater effect on devices’ performance because of the scaling effect.

Electrospray devices are applied for diverse functions with small amount of liquid. Thus a capillary with small inner diameter is used for the emitter. The angle and radius of the emitter nozzle tip affects the performance of an emitter. Reducing the tip radius and tip surface area will reduce the size of the fluid cone during electrospray, resulting in the reduction of the dead volume[22].

3.1.4 Length and Inner Structure

The electric field near each nozzle is not identical because of edge effects. This nonuniformity leads to an uneven electrostatic pulling force on the liquid among the nozzles, yielding different flow rates from one emitter to another.

The solution is to make the viscous pressure drop across each nozzle dominant over the electrostatic pulling force, which is comparable to the capillary force $\gamma/r$, where $\gamma$ is the liquid surface tension and $r$ is the nozzle tip radius[24]. As the nozzle diameter is reduced to minimize the propellant evaporation, the pressure drop required increases rapidly. Therefore, a flow homogenizer with high flow impedance is needed to achieve uniform feeding of low flow rate of propellant to each thruster. One existing but unsatisfactory approach (Figure 5) is to create artificial porous media structure by filling silica beads of ~2 μm inside the nozzle. It requires
labor-intensive process and the reproducibility from nozzle to nozzle or from device to device may be limited.

Figure 5 Emitter with artificial porous media structure[25]

According to the microfluidic mechanism, the flow impedance is proportional to the channel length. Existing designs are out-of-plane and the channel length is limited by the thickness of the wafer, which is ~500 μm.

We intended to design and fabricate an in-plane structure to increase the channel length. In addition, the plane design allows us to integrate more sophisticated microfluidic features that further increase the flow impedance while reducing the clogging risks. Therefore, we propose to use an array of micropillars with high aspect ratios. One characteristic length is the height of the pillars, which can be reasonably tall (on the order of 50 μm). This will avoid complete blockage
of the channel, therefore the clogging risks are reduced. The other characteristic length is the gap between two cylindrical pillars (Figure 6). By reducing the gap, a very high pressure drop can be expected[26].

![Figure 6 Emitter nozzle with high aspect ratio micro pillars](image)

**3.2 Simulation**

With all the considerations mentioned above, a photomask for the emitter is designed with detailed parameters shown in Figure 7.
In order to ensure the emitter’s strength, the wall of the nozzle is designed to be relatively thick. The pillars are designed with the same radius of 15μm. The gap between them is 10μm. With the design parameters, a pressure field simulation was conducted to predict the performance of the emitter.
3.2.1 Pressure Field

Figure 8 Simulation result of pressure field in the nozzle (in Pa)
A pressure field simulation in Figure 8 result shows that the liquid pressure drops gradually and smoothly across the nozzle from inlet to outlet. Thus, we can expect a viscous pressure drop (1000Pa) across each nozzle dominant over the electro-hydrodynamic pulling force.
3.2.2 Velocity distribution

Figure 9 Flow velocity distribution (in m/s)

A liquid flow velocity distribution simulation result in Figure 9 shows that besides the portion around the pillar and nozzle outlet, the flow velocity is uniform across the nozzle. According to this simulation result, embedded structures could achieve uniform feeding of low flow rate of liquid to each emitter.
3.3 Fabrication

3.3.1 Photolithography

The simulation results show a lot of promise in terms of the emitter’s performance. Therefore we proceeded to the fabrication steps according to our design. Starting from a 3 inch thermally oxidized silicon wafer, an Au/Ti thin film was deposited. AZ 40XT (Microchemicals GmBH, Germany) photoresist was applied and spin-coated at 800 rpm for 30 sec and baked at 75°C for 120sec, at 105°C for 120 sec, and at 125°C 180 sec, subsequently. The substrate was exposed to UV (I-line) using an aligner (EVG 620, EV Group, Austria) for 32 sec with a soft-contact (~10um gap). Post-exposure baking (PEB) was done at 75°C for 20 sec and at 105°C for 160 sec. Finally the exposed substrate was developed in a developer (AZ300MIF-1G, Microchemicals GmBH, Germany) for 4 min. After rinsing the substrate, photo defined patterns were inspected with a microscope before electroplating.

3.3.2 Electroplating

The exposed area with a metal seed layer of Au/Ti was used as a cathode that was to be electroplated. For a current source, a pulsed power supply (DUPR 10-1-3, Dynatronix) was used. For an anode, a nickel plate was used. First, a nickel striking was conducted with a current density, 10mA/cm² for 10 min at ~25°C. Nickel striking bath is consisted of 100g NiCl₂, 450ml H₂O and 50ml HCl. After rinsing in DI water, Ni plating was done using a commercially available Ni sulfamate bath (Nickel Sulfamate RTU, Technic Inc.) with a current density,
10mA/cm² for 20 hrs at 55°C. Throughout the electroplating process, the duty cycle was kept at ϕ=0.5. Finally, photoresist was removed in acetone, leaving behind a metallic structure.

A schematic view of the bottom layer fabrication process is shown in Figure 10.

Figure 10 Bottom layer fabrication. (a) Au/Ti seed layer deposition, (b) photoresist patterning, (c) Ni electroplating and (d) photoresist stripping.

PR pattern works as a mold by which electroplating proceeds only in the patterned area that follows the design. At a constant current density, metal layer is built up gradually until it reaches the required thickness. Then the PR is stripped by acetone and bottom layer is left on the substrate and ready for the next step fabrication.
**Figure 11 Alignment procedure for pillar and side wall structures**

After the bottom layer is fabricated, the pillar structure and top layer was fabricated on the base of the bottom layer. This process also starts from the PR patterning. After spin coating a layer of PR on the substrate with fabricated bottom layer, the mask of pillar structure was aligned to the bottom layer as shown in Figure 11. Using the UV aligner, substrate’s position was adjusted in reference to alignment marks on the bottom layer and the mask for the second layer was aligned and exposed.
Figure 12 Fabrication process of inner structure and top layer. (a) Fabricated bottom layer, (b) photoresist patterning, (c)-(f) Ni electroplating and (g) photoresist stripping and device releasing.

After the alignment, almost the same process as bottom layer fabrication was carried out. After finishing the PR patterning (Figure 12 (b)), the wafer was immersed in deionized (DI) water and then put in the desiccators with vacuum to remove trapped air bubbles in deep areas. As Figure 12 (c) and (d) show, after the plated pillar structure reaches the top of the PR, it grows in all directions at the same rate so that a mushroom shape forms (Figure 12(e)). With the growing of “mushrooms”, they finally touch each other and then form a cap to seal the emitter’s top opening (Figure 12(f)) so that an enclosed structure is fabricated. The device is separated from the substrate by dissolving the PR in acetone and etching the Au/Ti underlayer (Figure 12(g)).

The final fabricated device is shown in Figure 13.
3.4 Test

During the whole process of fabrication, emitters were inspected after each fabrication step to make sure the process follows the design. After the emitters were fabricated, a series of tests were conducted to characterize the performance of emitters.

3.4.1 Optical Inspection

The fabrication processes were monitored by profilometer (Alphastep 200 Profilometer, Tencor), optical microscope, and scanning electron microscope (SEM).
Figure 14 Measurement of surface profile

As shown in Figure 14, a profilometer was used to measure the thickness of metal layer precisely. After the first few hours of electroplating, the metal layer’s thickness was measured to estimate the growth rate and then an estimated plating time to completion could be calculated.

The plating process was monitored every two hours. Using an optical microscope, we inspected whether metal was plated inside the PR pattern, whether the whole device was plated uniformly and whether there are any abnormally plated structures.

According to the initial observation results, some adjustments were made such as supplying the bath solution or changing the bath temperature and current density. The conditions described in the fabrication section were optimized ones based on these experiments.

Main features in micron scale were observed with SEM to inspect details of the fabricated devices.
3.4.2 Electrospray Test

![Functional test setup](image)

**Figure 15 Functional test set up: (a) schematic view and (b) actual view.**

As shown in Figure 15, a “sandwich” fixture was prepared and used for testing. The fixture was designed so that air or liquid may enter through the inlet of top enclosure and then come out from the opening of an emitter. O-ring was used for sealing between a cap and the emitters.

Before the actual electrospray test, in order to determine if the passage through the prepared device is cleared or clogged, the whole setup was immersed in water and air was aerated through the inlet. After this verification, a liquid (alcohol for testing) was pumped into the inlet and a high DC voltage was applied between the emitter tip and a ground electrode.
3.5 Results and Discussion

3.5.1 Electroplating Rate

The thickness of nickel layer was measured as a function of time as shown in Figure 16.

![Figure 16](image)

**Figure 16** Thickness of electroplated structure as a function of time

With the given conditions, the rate of growth was 40μm/hr - 20μm/hr. The growth rate decreased gradually. During the process of electroplating, the surface of metal layer is smooth at first and becomes more and more rough as the electroplating proceeds. As a result, this increased surface area of the metal layer reduces the effective current density smaller than expected. This can be considered as one reason for the reduced growth rate. The consumption of metal cations in the plating bath during the plating also may be a factor. However, since the solution was replenished regularly, this may not be a major reason.
3.5.2 Fabrication results

3.5.2.1 Bottom layer

![Fabrication results: (a) after PR patterning, (b) after striking treatment and (c) after electroplating.](image)

We could observe throughout the process metal layer follows the PR pattern faithfully but with small deformation at the corner area due to a faster growth in that location which induces slight deformation of soft PR. Figure 17 (b) shows that nickel striking treatment produced a very uniform thin seed layer of nickel with high quality and good adhesion to the substrate. The Ni striking step cleaned the surface of the substrate with the acid in the solution. On the base of the striking layer, a layer of nickel around 70 μm was plated with nickel sulfamate based bath. The adhesion of bottom layer to the substrate was good and no detachment or warping was observed.

The nickel striking treatment usually use a higher current density than normal electroplating, which plates a thin layer if nickel with a high residual stress. Thus, an appropriate current density and a striking time are important to prevent detachment of the film.
3.5.2.2 Top layer and cap formation

The top layer with micropillars and a nozzle cap were electroplated on the bottom layer.

![Top layer and cap formation](image)

**Figure 18** Top layer and cap formation: (a) patterned PR, (b) formation of micropillars, (c) formation of mushroomed cap layer (d) enclosed device.

Micropillar patterns were electroplated concurrently with side wall structures. No large deformation of patterns was observed. It is known that nickel sulfamate based bath produces a low residual stress nickel structure[18]. For top layer fabrication process, the most difficult step was PR patterning as Figure 18 (a) shows. Because the size of pillar pattern is very small that has a radius of 15 μm but a height of 70 μm, inappropriate developing led to several defective patterns as shown in Figure 19 and Figure 20.
Figure 19 Defective pattern formation. (a), (b) underdeveloping and (c) overdeveloping. In Figure 19 (a) and Figure 20 (a) and (b), PR is not developed completely. In such case, the opening is insulated by PR and patterns cannot be electroplated. In Figure 19 (b) and (c), a slant sidewalls are formed which deviate from the intended design.

Figure 20 Defective patterns resulted from underdeveloping.
3.5.3 SEM observation

Figure 21 SEM pictures of (a) layer after Ni striking, (b) bottom layer, (c) micropillars and side walls near the nozzle tip, and (d) micropillars in the middle.

SEM pictures clearly show that the enlarged view of striking layer, bottom layer and the array of pillars. A finished emitter nozzle was cut in the middle to observe the inner structure.
Figure 22 Inner structure of fabricated emitter. (a) Broken nozzle, (b) and (c) side view of a fractured nozzle portion.
Figure 22 shows that the sidewalls and pillars could be integrated into an enclosed emitter by electroplating. The height of the pillar is around 50 μm and the radius is around 15 μm as designed. The gap between the pillars is around 10 μm.

3.5.4 Emitter functions

Before electrospray test, the emitter was immersed in water and aerated with air. Bubbles came out of the nozzle tip which proved the clear passage within the emitter.

![Image](image.png)

**Figure 23** Formation of a air bubble at the tip which verifies the clear passage within an emitter.

When a high DC voltage was applied between the emitter tip and a ground electrode, the emitter started to jet in a stable mode. In addition, the emitter nozzle was bent intentionally to different angles in order to verify the multi-directional jetting capability.
Figure 24 Formation of a jet at the emitter tip

When the applied voltage increased to around 2-3 kV, a stable cone forms and starts to jet continuously. After jetting for some time, the liquid accumulates on the ground electrode and forms another cone and jets back. The cone formed at the tip has an angle of 83°.

A flexing capability of the emitter was demonstrated by attaching the emitter to a string and deflecting it while the jet was formed. Figure 25 shows the emitter could flex by 26° without fracture.
Figure 25 Multi-directional jetting. (a)-(f) the emitter jets continuously and consistently with different flexing angles from $0^\circ$ to $26^\circ$.

The emitter worked with a good mechanical integrity in different directions without failure. This result demonstrates the usability of the emitter for flexing jets that could be applied to redirecting flying bodies. Even with a large angle bending, the emitter continuously created jet as intended.
CHAPTER FOUR: NANO STRUCTURED METAL FILMS FOR PHOSPHATE SENSORS

4.1 Design Requirements

4.1.1 Background

In hydroponics and agriculture, fertilizers applied to maximize yield and quality. As an essential nutrient for plants, phosphate is widely used in these fertilizers, which also leads to environmental problems such as undesired growth of the algae and other aquatic vegetation and the eutrophication of natural water bodies. Therefore, people need to measure the phosphate in water to control these problems. With this, the development of simple and compact phosphate sensors is becoming more important[27].

Based on the formation of Co₃(PO₄)₂ precipitate on a Co (Cobalt) layer, phosphate can be measured directly. The sensing mechanism is a two step process: dissolution of cobalt on the electrode surface and the formation of oxide film[28]:

\[
\begin{align*}
2Co + 2H_2O &\leftrightarrow 2CoO + 4H^+ + 4e^- \\
O_2 + 4H^+ + 4e^- &\leftrightarrow 2H_2O \\
2Co + O_2 &\leftrightarrow 2CoO
\end{align*}
\]

When the sensor is immersed in the solution containing phosphate, cobalt phosphate is formed on the electrode surface[28]:

\[
\begin{align*}
3CoO + 2H_2PO_4 + 2H^+ &\leftrightarrow Co_3(PO_4)_2 + 3H_2O \quad \text{(at pH 4.0)} \\
3CoO + 2H_2PO_4 + 2H_2O &\leftrightarrow Co_3(PO_4)_2 + 4OH^- \quad \text{(at pH 8.0)}
\end{align*}
\]
\[ 3\text{CoO} + 2\text{PO}_4^{3-} + 3\text{H}_2\text{O} \rightarrow \text{Co}_3(\text{PO}_4)_2 + 6\text{OH}^- \text{ (at pH 11.0)} \] (6)

These reactions give a voltage output related to the phosphate concentration[29].

Inspired by the nanostructure of alloys, we propose to electroplate a layer of Co-Cu alloy and then obtain nanoporous Co electrode through selective etching of Cu (Copper). This nanoporous Co electrode can be expected to perform better than a planar Co electrode due to the increased surface area.

**Figure 26 Co-Cu alloy phase diagram**[30].

As the phase diagram (Figure 26) indicates, Co and Cu are completely miscible at low temperature which makes this alloy system well suited for pulse-electroplating over a wide concentration range[31].

According to the research on pulse electroplating of Co-Cu, the microstructure of the alloy is closely related to the electroplating parameters[32]. In the electroplating bath solution, Cu has a
much smaller concentration than Co so that the deposition rate of Cu is mass transport controlled. During the pulse-on time, a current density which is much larger than the limiting current of Cu is applied. Co and Cu are deposited on the substrate spontaneously. Besides the depositing process, the Cu ions also undergo a displacement reaction with deposited Co during the pulse-off time. In this way, after a few pulses the Co ions will be depleted in the Nernst layer. Under both the effects of electroplating process and displacement reaction, a Co-Cu alloy with nanostructure is deposited on the substrate. Research results show that the optimized microstructure is obtained with short-cycle time and a duty cycle of 0.2[32].

4.2 Fabrication

The fabrication process is relatively simple with three steps: photolithography, electroplating and selective etching.

4.2.1 Photolithography

Starting from a 3 inch thermally oxidized silicon wafer, an Au/Ti thin film was deposited. Microposit S1813 (Shipley Company) photoresist was applied and spin-coated at 3000 rpm for 50 sec and baked at 110°C for 180 sec, subsequently. The substrate was exposed to UV (I-line) using an aligner (EVG 620) for 8 sec with a soft-contact (~10um gap). Then the exposed substrate was developed in a developer (MIF CD-26, Shipley Company.) for 40 sec. After rinsing the substrate, photo-defined patterns were inspected with a microscope. Finally, the substrate was hard baked at 110°C for 10 min.
4.2.2 Sensor Electrode Fabrication

Figure 27 Sensor electrode layer fabrication process: (a) Au/Ti seed layer deposition, (b) photoresist patterning, (c) Co-Cu alloy electroplating, (d) photoresist stripping, and (e) selective etching of Cu to form a nanoporous electrode layer.

As shown in Figure 27, electroplating of Co-Cu alloy proceeds within the PR patterned area. According to the research result of pulse plating of Co-Cu alloy, the current density is set as 75mA/cm$^2$ and duty cycle as 0.2 ($t_{on}=2$ms) and the bath solution consisted of 0.7 M CoSO$_4$·7H$_2$O, 0.025 M CuSO$_4$·5H$_2$O, 0.18 M Na$_3$C$_6$H$_5$O$_7$·2H$_2$O and 1/50 part of Saccharin[31]. Citrate is used as complexing agents to plate a smooth deposits[33] through leveling action[34]. Saccharin is used as wetting agent so that hydrogen bubbles produced during plating will not stick to the substrate surface, which eliminates the formation of pits[31]. After electroplating 10 minutes, a layer of alloy around 1.7 µm thick was deposited. Then the PR was stripped and
another PR patterning was used for a connection line and a contact pad. After the contact pad was formed, a selective Cu etchant (250 ml aqueous solution containing 4 g of CuSO$_4$·5H$_2$O + 100 ml of NH$_4$OH) was used to remove Cu in the alloy so that only nanoporous cobalt was left.

As Figure 28 (a) shows, the sensor consists of an electrode, a connection line and a contact pad. The electrode is designed in a circular shape with a diameter of 4 mm.

With a fabricated sensor chip, a silver paste was used to connect the chip to a printed circuit board (PCB) carrier. The whole chip except the electrode area was encapsulated with epoxy for insulating from a test solution. The schematic view of the fabricated and packaged chip for testing is shown in Figure 28(b).

**Figure 28** Schematic view of a sensor device. (a) Fabricated chip and (b) packaged device.
4.3 Test

4.3.1 Optical Inspection

In order to characterize the fabrication process and sensor performance, a sensor electrode before selective etching, after selective etching and a pure cobalt electrode were prepared. Surface morphologies were observed by atomic force microscopy (AFM) and SEM.

After comparing the surface morphologies, we adjusted the plating time, etching time and current density to obtain optimized results.

4.3.2 Phosphate Sensing

The phosphate sensor electrodes were tested with standard KH$_2$PO$_4$ solutions with concentrations range from 10$^{-1}$ M to 10$^{-7}$ M at ambient temperature. The pH of these standard solutions were adjusted to around 7.5 by adding potassium hydroxide[16].

A phosphate sensor chip was connected with an Ag/AgCl reference milli-electrode (MI-401, Microelectrodes Inc.). Before testing, the sensor chips were immersed into DI water for around 24 hours to form a CoO (cobalt oxide) layer on the electrode surface. Then both electrodes were immersed into solutions with stirring until a steady-state potential was observed (Figure 30). The potential between the two electrodes was monitored by a millivolt (mV) meter (Model 215, Denver Instruments)[35].
Figure 29 Experiment setup. (a) schematic view and (b) actual view.
4.4 Results and Discussion

4.4.1 Fabrication results

Figure 30 AFM results of electrode fabricated with different current density: (a) 75mA/cm$^2$, (b) 120mA/cm$^2$ and (c) 150mA/cm$^2$.

The AFM results show that the roughness decreases when the current density increases. During the pulse-off time, Co is not electroplated and plated Co has a displacement reaction with Cu ions. The composition of Co is mainly decided by the current density during the pulse-on time. The larger current density is applied, the more Co is plated in the alloy and less Cu conversely. Thus, during the selective etching of Cu process, less Cu is removed from the alloy, which results in a more smooth surface.
Based on the AFM characterization results, 75mA/cm² current density produced the roughest morphology, which can be translated into a larger surface area. Therefore, electrodes fabricated with 75mA/cm² current density were used for further characterization. Energy dispersive spectrometry (EDS) was used to measure the Cu composition in the electrodes fabricated with different etching times.

Figure 31 EDS measurement. (a) 5s etching and (b) 10s etching.
The amount of Cu decreased when the electrode were etched for a longer time as expected. In order to increase the surface area, Cu needs to be removed from the alloy. However, an excessive etching time caused electrode to peel off from the substrate. Based on this observation, the adequate etching time was found around 10s.

The electrodes fabricated with an optimized current density and etching time were observed with SEM to get details about the surface morphology.

![SEM pictures](image1)

**Figure 32** Sensor electrodes surface morphology SEM pictures. (a) Co-Cu alloy before etching, and (b) after etching.

In Figure 33, both electrodes were fabricated with 75mA/cm² current density and same bath solution. SEM pictures show clearly that before selective etching the alloy layer has a smooth surface. After the selective Cu etching, the surface becomes rough with nanoporous textures. This proves that during electroplating process Co and Cu are co-electroplated to form the alloy
with a smooth surface and that the selective etching could successfully remove Cu from the alloy and leave behind Co with nanoporous textures.

With all these characterization results, we can expect a better performance of the electrodes with the nanoporous Co structure.

4.4.2 Sensor Functions

In order to characterize the sensor’s detection range, we prepared KH$_2$PO$_4$ solutions with concentrations range from $10^{-7}$ M to $10^{-1}$ M. A nanoporous Co was used as a working electrode and pure planar Co electrode fabricated with the same parameter was used as a control sample. According to the theory of electrochemistry, the potential measured on the electrode is governed by the Nernst equation:

$$E_{cell} = E^0 + \frac{RT}{nF} \ln (K_{eq})$$  \hspace{1cm} (7)

where $E_{cell}$ is the measured potential, $E^0$ is the standard potential for the whole cell reaction, R is universal gas constant, F is Faraday constant, $K_{eq}$ is reaction quotient and n is number of moles of electrons transferred in the cell reaction. At room temperature (298K), $RT/F$ can be replaced with 25.693 mV. By changing the natural logarithm to base 10 logarithm, we get:

$$E_{cell} = E^0 + \frac{0.5916V}{n} \log_{10} (K_{eq})$$  \hspace{1cm} (8)

that the potential is decided by the reaction quotient $K_{eq}$.

When the Co sensor electrode is immersed in DI water, the base line potential is developed based on:
When phosphate is present in the water, it will combine with CoO and a new balance will be reached as in (4)-(6). The reaction quotient for the new equilibrium is (at pH 8.0):

\[
K_{eq} = \frac{[\text{CoO}]^2}{[\text{Co}]^2[\text{O}_2]} \tag{9}
\]

At a fixed stirring speed and pH, every factor except the concentration of HPO\(_4^{2-}\) can be considered as constant, so that we can expect a shifted potential in the form of:

\[
E = E_0 + m \log([a]) \tag{11}
\]

m is the slope, and a is the activity of the measured ion species\[36\]. For estimation, we assume the solution is ideal solution so that solution activity equals to the concentration. Therefore we expect a linear relation between electrode potential and \(\log[\text{KH}_2\text{PO}_4]\). Figure 34 shows a measured potential as a function of phosphate concentration. The test result shows that both electrodes performed as Nernst equation describes. However, the electrode with nanoporous structure has a larger detection range and signal (negative potential), compared to the planar Co electrode.
In addition, compared to the reported needle type cobalt sensor which has a test range from $1 \times 10^{-5.1}$ to $1 \times 10^{-3}$ M[14], the nanoporous sensor shows a wider test range from $1 \times 10^{-7}$ to $1 \times 10^{-1}$ M. The nanoporous structure enhances the electroactive surface area of the electrode. Therefore, accessible sites for the redox reaction increase by a large extent. This contributes to the improved sensor response.

**Figure 33** Sensor electrode test results. (■: Planar Co electrode; ○: Nanoporous electrode)
CHAPTER FIVE: CONCLUSION AND FUTURE WORK

5.1 Conclusion

Using customized pulsed electroplating methods, high aspect ratio embedded microscale features and high surface area nanoporous structures were designed and fabricated. Their functionalities were demonstrated in flexible electrospray emitters and phosphate sensors.

Based on the design requirements and simulation results which show a large and dominant viscous pressure drop across each nozzle over the electro-hydrodynamic pulling force and uniform feeding of a low flow rate liquid, the emitters were fabricated with an optimized set of photolithography and plating parameters.

For the electrospray emitter fabrication process, two layer photolithography was used to fabricate device’s bottom layer, embedded micropillars and top layer. A thick photoresist was used for electroplated molds and conformal growth during overplating was utilized for enclosing the emitter autonomously. Nickel sulfamate bath yielded a low stress mechanical structure. Emitters could be fabricated with a long channel (4.3mm) and integrated micropillars (with a radius of 15 μm and a height of 50 μm). A clear passage through the emitter without clogging was first verified with an aeration test.

The emitter under the applied voltage, 2-3kV, could form a stable cone jet continuously. The cone formed at the tip has an angle of 83°. The flexing was demonstrated with up to 26° bending angle due to the elastic nature of plated nickel. This result demonstrates the usability of the emitter for flexing jets that could be applied to redirecting flying bodies.
In the second part of thesis study, thin cobalt-copper metal alloy films were electroplated on a silicon substrate and copper was selectively etched to fabricate nanoporous electrodes. A thin alloy film (t~1.7 μm) was electroplated from an electroplating bath solution contains both sulfate salts of cobalt and copper, as well as addictive agents to increase the quality of plated alloy. The pulse current duty cycle was set to 0.2 and density was optimized to 75mA/cm². After the electrode was plated on the substrate, a copper sulfate based etchant was used to selectively etch copper from the alloy to obtain a nanoporous cobalt structure. The surface morphologies were observed with AFM and SEM. Fabricated sensors were packaged and tested in standard KH₂PO₄ solutions with phosphate concentrations. Compared to a planar cobalt electrode, the nanoporous cobalt electrode showed improved signal intensity and, detection range (1×10⁻⁷ to 1×10⁻¹ M). The increased surface area and relatively simple fabrication protocols make the proposed method attractive and promising for many environmental sensing applications.

5.2 Future Work

Besides the multi direction jet test, more tests and measurement such as pressure drop, relation between voltage and current will be carried out to characterize the performance of the emitter in different aspects. Multiplexing emitters will be an interesting research topic as an extension of the current research in order to test the concurrent or sequential formation of jets.

For the phosphate sensor electrodes, electroplating parameters need to be further optimized to address the detachment of nanoporous structures. A combination of various current densities, duty cycles and etching times can be used to study electrode morphologies and corresponding performances as sensing electrodes.
APPENDIX A: ELECTROPLATING OF EMITTER
This appendix contains the detailed process steps for the electroplating of electrospray emitters.

Substrate: 3 inch (111) Si wafers with Au/Ti seed layer, \( t = 250 \, \mu m \)

1. Base clean.
2. Spin coat AZ40 XT photoresist (30 sec. at 1000 RPM) for 70 \( \mu m \) thick patterns.
3. Let sit at room temperature for 5 minutes.
4. Soft bake: hot plate at 75 °C for 2 minutes with cap, hot plate at 105 °C for 2 minutes with cap, hot plate at 125 °C for 3 minutes with cap.
5. Let sit at room temperature for 5 minutes.
6. Align and expose. Exposure time is 32 seconds at 12 mW/cm\(^2\).
7. Develop for 3 minutes in a developer (AZ300MIF-1G).
8. Nickel striking for seed layer and adherence. Current density is 10 mA/cm\(^2\) for 5 minutes.
9. Electroplating of nickel bottom layer from nickel sulfamate based electroplating bath. Current density is 10 mA/cm\(^2\) for around 15 hours.
10. Remove photoresist using acetone-methanol-DI water.
11. Second layer.
12. Spin coat AZ40 XT photoresist (30 sec. at 800 RPM) for 80 \( \mu m \) thick patterns.
13. Let sit at room temperature for 5 minutes.
14. Soft bake: hot plate at 75 °C for 2 minutes with cap, hot plate at 105 °C for 2 minutes with cap, hot plate at 125 °C for 3 minutes with cap.
15. Let sit at room temperature for 5 minutes.

16. Align and expose. Align the second layer mask to the bottom layer pattern. Exposure time is 32 seconds at 12 mW/cm².

17. Develop for 3 minutes in a developer (AZ300MIF-1G).

18. Clean with DI water and dry with nitrogen gas.

19. Keep the wafer merged in DI water within a patri dish and put into desiccators with vacuum to remove tracked air bubbles in patterns. Vacuuming time is 30 minutes.

20. Electroplating of second and top layer from nickel sulfamate based electroplating bath.

   Current density is 10 mA / cm² for around 25 hours.


22. Detach the fabricated emitter through etching Au/Ti seed layer by Au etchant and Buffered Oxide Etch (BOE).

23. After detaching the emitter, keep it merged in acetone with ultrasonic cleaning for 1 hour.

**Note:** Photolithography conditions for AZ40 XT photoresist is extremely dependant on humidity. The conditions given in this appendix are for processing under the relative humidity (RH) of 50% or higher.
APPENDIX B: ELECTROPLATING OF PHOSPHATE SENSOR
This appendix contains the detailed process steps for the electroplating of electrospray emitters.

Substrate: 3 inch (111) Si wafers with Au/Ti seed layer, $t = 250 \, \mu m$

1. Base clean.
2. Spin coat Shipley 1813 photoresist (10 sec. at 500 RPM 47 sec at 3000 RPM) for 1.3 $\mu m$ thick patterns.
3. Let sit at room temperature for 3 minutes.
4. Soft bake: hot plate at 110 °C for 3 minutes with cap.
5. Let sit at room temperature for 3 minutes.
6. Align and expose. Exposure time is 8 seconds at 12 mW/cm$^2$.
7. Develop for 40 minutes in a developer (MIF CD-26).
8. Electroplating of sensor electrode layer from electroplating bath. Current density is 100 mA / cm$^2$ for around 15 minutes.
9. Remove photoresist using acetone-methanol-DI water.
10. Put the wafer in selective copper etchant for 10 seconds and clean with DI water.
11. Second layer.
12. Spin coat Shipley 1813 photoresist (10 sec. at 500 RPM 47 sec at 3000 RPM) for 1.3 $\mu m$ thick patterns.
13. Let sit at room temperature for 3 minutes.
14. Soft bake: hot plate at 110 °C for 3 minutes with cap.
15. Let sit at room temperature for 3 minutes.
16. Align and expose. Align the second layer mask to the bottom layer pattern. Exposure time is 8 seconds at 12 mW/cm$^2$.

17. Develop for 40 seconds in a developer (MIF CD-26).

18. Clean with DI water.

19. Remove photoresist using acetone-methanol-DI water.
LIST OF REFERENCE


[8] S. Beeby, G. Ensell, M. Kraft, and N. White, 

[9] J. Dufour, 

 *Theory and practice of pulse plating*.


