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Electrode Integration of Nanostructured Metal and Metal Oxide Materials Based on in-situ Growth Methods for Environmental Sensors

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ELECTRODE INTEGRATION OF NANOSTRUCTURED METAL AND METAL OXIDE MATERIALS BASED ON IN-SITU GROWTH METHODS FOR ENVIRONMENTAL SENSORS

by

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M.S. University of Central Florida 2014
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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Materials Science and Engineering in the College of Engineering and Computer Science at the University of Central Florida
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Major Professor: Hyoung Jin Cho
ABSTRACT

In the past decades, increased human population and activities have introduced a large amount of pollutants into the environment. Various types of conventional analytical instruments were used for monitoring the emitted chemicals with low detection limit, high accuracy, and discrimination power. However, many of these methods are laboratory-based owing to sample collection, transportation, extraction, and purification steps.

To make real-time on-site monitoring possible, miniaturized sensors with various integrated elements were developed. One of the most well-known strategies is to utilize nanostructured materials with enhanced sensing properties for those devices. For a majority of the current state of art devices, the synthesis of nanostructured materials and device integration are done separately, that is, “synthesis first and then integration” approach which involves two separate process steps. However, this approach comes with some disadvantages such as misalignment, contamination, as well as disconnection between nanomaterials and electrodes.

To overcome the aforementioned technical challenge, several synthesis methods were developed and validated for in-situ integration of nanostructured metal and metal oxide materials for environmental sensors in this work. The electroplating technique combined with photolithography was used to make the predefined metal electrodes. Then, with subsequent post-treatments, nanostructured metals and metal oxides could be produced in-situ and directly integrated in the electrodes without any extra transfer process steps.

In the process of developing a phosphate sensor, nanofibrous Co electrodes were fabricated by pulsed electroplating of Co-Cu alloy and dealloying the Cu component. A linear potentiometric response to phosphate in the $10^{-5}$ to $10^{-2}$ M concentration range was obtained which validated the sensor’s function. A
mechanism based on mixed potential response was proposed to elucidate the Co electrode behavior in aqueous solutions with varying pH conditions and optimum pH ranges for working devices were proposed. In addition to the alloying and dealloying method, the template assisted electroplating method was also investigated. A nanoporous Co-Cu electrode fabricated by electroplating through a sacrificial glass fiber template was obtained. A linear amperometric response to phosphate with suppressed oxygen interference was achieved in a $10^{-5}$ to $10^{-2}$ M concentration range of phosphate. An analysis of the cyclic voltammetry characterization results provided a direction for further exploring an optimized electrode polarization potential range for suppressing oxygen interference while maintaining a good sensitivity to phosphate. Based on this result, we improved the fabrication process with another template: in-situ hydrothermally grown ZnO nanoflakes on the electrode surface, as a template for uniform nanostructured Co electroplating. The cyclic voltammetry characterization of the fabricated electrode showed an amperometric response in the range of $10^{-6}$ to $10^{-2}$ M of phosphate where the limit of detection (LOD) was enhanced compared with the previous work.

For the flammable gas sensor development, the in-situ oxidation of Cu was utilized to form nanowires for sensing electrode fabrication. Multiple CuO nanowires were synthesized in-situ on the electroplated interdigitated Cu electrodes on a hotplate at 500 °C in air. The nanowires were successfully integrated as a sensing element into the device, forming bridges between two electrodes. The sensor’s behavior was characterized by a current-voltage measurement. Simple processing parameters could be utilized for controlling the electrode morphologies and determining the characteristics of contacts - Schottky or Ohmic - at the electrode interface. A hypothesis was proposed to explain the transition phenomenon between Schottky and Ohmic contact modes, providing an important baseline for future device design and fabrication. Finally, the fabricated sensor was tested for a flammable gas detection using saturated ethanol vapor at room temperature, which implicates a low power consumption gas sensor without elevating the sensor temperature unlike traditional gas sensors.
ACKNOWLEDGMENTS

At the beginning of this dissertation, I mostly want to express my gratitude to my advisor and mentor, Prof. Hyoung Jin Cho. Research life is difficult; every little progress and innovation is based on many trials and failures. The most important thing I learnt from my advisor is patience without losing enthusiasm. During the past four years of research as a PhD candidate, Dr. Cho gave me unconditional support, guidance and encouragement. I am impressed not only by his knowledge and ability in science research but also by his rigorous academic attitude. We met many failures, but we also made great efforts together to gain achievements through these failures. It is my honor to be a part of his group.

I also want to thank the lab members, Dr. Sanghoon Park, Christopher Hughes and Alireza Karbalaee. From our scientific discussions, we generated many great ideas. Thanks for their suggestions and encouragement when I met difficulties; their friendships are precious to me. I also thank our collaborators, Xiangmeng Ma, Jared Church, Samuel Rhodes and Zhao Ma, for supporting me in the research process.

Thanks also to my committee members, Prof. Jiyu Fang, Prof. Linan An, Prof. Lei Zhai and Prof. Andrew Dickerson, for evaluating my work and for their constructive comments and discussions. Their different backgrounds and profound knowledge expanded my views and provided solid support for my research.

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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>HPLC</td>
<td>High-Performance Liquid Chromatography</td>
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<tr>
<td>GC-MS</td>
<td>Gas Chromatography–Mass Spectrometry</td>
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<tr>
<td>C/PVD</td>
<td>Chemical/Physical Vapor Deposition</td>
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<tr>
<td>AAO</td>
<td>Anodic Aluminum Oxide</td>
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<td>MEMS</td>
<td>Microelectromechanical Systems</td>
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<td>E-beam</td>
<td>Electron Beam</td>
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<td>PR</td>
<td>Photoresist</td>
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<tr>
<td>HAB</td>
<td>Harmful Algae Bloom</td>
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<tr>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
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<tr>
<td>ISE</td>
<td>Ion-Selective Electrode</td>
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<tr>
<td>CHEMFET</td>
<td>Chemically Modified Field-Effect Transistor</td>
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<tr>
<td>ITO</td>
<td>Indium-Tin Oxide</td>
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<tr>
<td>PEP</td>
<td>Pulsed Electroplating</td>
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<tr>
<td>EDS</td>
<td>Energy Dispersive Spectrometer</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>PCB</td>
<td>Printed Circuit Board</td>
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<tr>
<td>XPS</td>
<td>X-ray Photoelectron Survey</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<td>PORTE</td>
<td>Porous Template-based Electroplating</td>
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<td>BOE</td>
<td>Buffered Oxide Etchant</td>
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<td>CV</td>
<td>Cyclic Voltammetry</td>
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<td>Description</td>
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<tr>
<td>LOD</td>
<td>Limit of Detection</td>
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<td>TF-XRD</td>
<td>Thin Film X-ray Diffraction</td>
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<td>I–V</td>
<td>Current–Voltage</td>
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<td>RPM</td>
<td>Revolutions per Minute</td>
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CHAPTER ONE: INTRODUCTION

Sensory organs in human body are critical to survival and have evolved to detect and avoid external threats. For example, the skin can sense temperature to avoid excessively hot or cold environments to maintain normal function of body system; the nose can sense odors of harmful gases such as H₂S to avoid inhaling them; the eyes can sense light in a certain range of wavelengths to recognize food and avoid overexposure to strong sunlight. However, the evolution of the natural sensor systems is far behind the complexity of the ambient environment. Harmful odorless and colorless gases such as CO lead to 438 deaths annually in the United States [1]; UV light with a wavelength out of the visual range can cause skin cancer, threatening our lives [2]; low-concentration leakage of highly toxic chemicals in drinking water or air leads to serious accidents [3]. Moreover, these pollutants and byproducts generated by human activities, especially in manufacturing and agriculture sectors, already have become a global issue [4] at different scales through various routes such as wind and water flows, as briefly shown in Figure 1. To improve detection ability, various chemical analysis methods such as high-performance liquid chromatography (HPLC) or gas chromatography–mass spectrometry (GC-MS) with high accuracy and sensitivity have been developed in the past. However, these methods are time consuming owing to the requirements of sample collection, transportation, extraction and purification processes. Therefore, in the past decades, great efforts have been devoted to high-quality environmental sensor and sensor network development [5] for on-site environment monitoring, early warning and tracking. Environmental sensor materials and devices have been studied actively in this context.
Figure 1 Schematic of chemical species spreading routes in natural environment under different scales.

For the material research aspect, the development of nanomaterials shows good promise toward sensor performance and quality improvement. Compared to conventional bulk materials, nanomaterials show enhanced electrical, optical, magnetic and catalytic properties owing to their increased specific surface area and reactivity. Various nanoscale features such as nanoparticles [6], nanopores [7], nanotubes [8], nanowires and nanorods [9] have been utilized for sensor applications. Specifically, nanostructured metals and metal oxides have drawn a large proportion of research interest owing to their unique applicability as catalyst [10], battery electrode [11], drug delivery [12] and sensing materials [13]. Many synthesis methods
for large-scale production have been studied and rapidly developed. For nanostructured metallic materials, their synthesis methods can be categorized into (a) reduction of a metal oxide with nanostructures [14], (b) alloying and dealloying [15], and (c) electrodeposition with template [16]. For nanostructured metal oxide material synthesis, wet chemical methods such as the sol-gel process [17], hydrothermal growth [18] and electro- [19] or electroless [20] plating are widely applied owing to their relatively simple procedures and mild experimental conditions compared to others that require high vacuum, high temperature, complex processes and expensive facilities such as chemical/physical vapor deposition (C/PVD) [21]. Researchers have found that by adjusting the synthesis parameters, reaction process kinetics can be tuned to achieve different nanostructures. Furthermore, sacrificial templates could be used to obtain specific morphologies. For example, metal oxide nanoparticles and films with nanoporous networks can be synthesized by thermal treatment of a precursor formed by a sol-gel process [22]; it was also reported that several metal oxide nanowires and nanorods could be synthesized by hydrothermal growth in aqueous solutions [9]; more straightforward, electro(less)plating with a template such as anodic aluminum oxide (AAO) is a common synthesis strategy for metal and metal oxide nanowire [23]. These achievements in material research enable the sensors to have a low detection limit, high sensitivity and good stability that rival conventional chemical analysis methods but are superior in terms of simple and fast detection.

On the other hand, to fulfill the requirements for in-time and on-site monitoring, early warning and tracking in large area, a large number of sensors must be deployed on site under different conditions and designed to communicate wirelessly to form the sensor network. However, in wilderness or aquatic environments where a sensor network is applied, it is ideal to minimize the frequency of maintenance requirements such as replacement of batteries. Therefore, power supply for long-term detection becomes a challenge. In recent years, with the development of microelectromechanical system (MEMS) technology, shrinking the size of the sensor configuration has become an attractive and effective strategy to reduce power consumption and provide a reliable package that greatly enhances the sensor’s lifetime.
However, the separate development in material science and device configuration has led to a technological gap in which the nanomaterials’ excellent qualities are not fully utilized in micromachined sensors. Only limited success of device integration but with high cost and a complex process has been reported [24, 25]. In these works, the procedure is mostly “synthesis first and then integration,” which involves additional steps for transferring synthesized materials onto preexisting electrode patterns. During the procedure, misalignment issues as well as contamination must be addressed to avoid degradation of microdevice performance. Moreover, the integration process is often labor-intensive and time consuming. With these limitations, the advantages of nanomaterials’ qualities are counterbalanced.
Therefore, the primary objective of this dissertation is to validate a pathway to bridge the gap by developing novel microdevice integration methods for nanoscale materials. Specifically, this work focuses on developing integration methods for environmental microsensors utilizing metals and metal oxides with
various nanoscale structures generated by an electroplating process and posttreatments. Compared to other metal deposition methods such as C/PVD that require a high vacuum environment, electroplating is a relatively simple wet chemical process that can be performed in an electrolyte solution with inexpensive equipment. The commonly used setup is shown by the schematic in Figure 2. 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 [26]. In some cases, the anode is an electrochemical soluble metal plate which is same to the one to be plated on the cathode. Both anode and cathode are immersed in the electrolyte solution consisted of one or several dissolved metal salts and sometimes other additives for buffering and tuning the electrolyte solution’s conductivity. During the electroplating process, the metal ions to be electroplated are reduced at the electrolyte and cathode interface. The metal electroplating rate at cathode surface is equal to the dissolving rate of anode, which is determined by the applied current density. In this way, the continuous dissolution of anode maintains the metal ions concentration in the electrolyte at a steady level [26]. In other cases, noble, insoluble metals such as platinum are used as a non-consumable anode. In these situations, ions of the metal to be electroplated will be depleted after a period of electroplating and must be replenished to assure the quality. This may be more economical when the metal salts are much cheaper than the metal itself.

For microsensor fabrication, the electroplating process is often performed on a silicon wafer as a plating substrate. Starting with a high-quality metallic seed layer deposited by electron beam (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 plating condition and the posttreatments influence the uniformity, morphology and composition of the deposited layer. Thus, the optimization of the electroplating and posttreatment conditions for successful microsensor application are developed and characterized in this dissertation.

In this dissertation, we developed and validated the methods based on electroplating techniques for in-situ formation of nanostructured Co and Co alloy electrode without involving any extra transferring process in
Chapter two to Chapter four. Compared with previous work, the effort in involving nanostructures and using different test methodology in our work improved the sensor’s performance in interference, limit of detection and stability. In Chapter five, we developed a new method for \textit{in-situ} formation of CuO nanowires by a simple oxidation process of electroplated Cu pattern. With this method, multiple CuO nanowire bridged interdigitated electrode was fabricated without any transferring process and was successfully applied for flammable gas sensing at room temperature with low power consumption.
2.1 Introduction

Figure 3 Phosphate cycle in the environmental system.

Phosphate plays a very important role in inorganic chemistry, biology chemistry and geological chemistry. It is one of the natural ingredients in almost all food and is widely applied as food additive [27]. This is because phosphate is an indispensable component and one of the most important electrolytes of all living organisms [28]. Therefore, in addition to application in food, phosphate is also widely used as fertilizer in agriculture [29]. In addition, phosphate has been applied as buffer solution in scientific research [30] and
as a binding agent in cement [31] and fire-proof materials [32]. All these demands have greatly promoted the mining and usage of phosphate.

However, owing to inappropriate over-mining and fertilization, phosphate is not efficiently consumed but leaks into natural water system through various routes in the phosphate cycle (Figure 3), leading to an accumulation of phosphate. Several serious environmental problems such as eutrophication and harmful algae blooms (HABs) that disrupt aquatic life cycles is mainly resulted by an increased phosphate concentration [33] in natural water systems. Moreover, it is hypothesized that the main reason of bio-deterioration of archaeological sites is phosphate enhanced over growth of cyanobacterial biofilms [34]. To solve and predict possibility of these issues, phosphate sensors for on-site and in-time measuring of exact phosphate levels are highly demanded [35]. Moreover, phosphate level determination methods can be further extended to clinical diagnosis [36, 37].

Based on the previously mentioned demands, several analytical methods have been developed such as spectrophotometry [38], chromatography [39], optical fluorescence- [40] and colorimetry- [41] based sensing, and electrochemical analysis [42] to measure the phosphate level in industrial, natural water and biological samples. Among these methods, spectrophotometric methods are limited for on-site detection involving complex facilities, extra agents, and extraction processes, whereas electrochemical analysis showed advantages in detection selectivity, stability and sensitivity. Further, electrochemical analysis methods are compatible with miniaturization and operation simplicity. Some prototype of electrochemical microsensors with simplified test procedures and fast response have already been developed, showing a great potential in on-site and in-time measurement [43]. Some commonly used electrochemical detection process and mechanism are summarized as follows:

- With an inert membrane such as polyvinyl chloride (PVC) membrane, the phosphate ion is first extracted into it from the sample solution and a steady potential is built up across the membrane.
By measuring this potential, the exact level of phosphate concentration can be determined through a calibration process. Some techniques such as chemically modified field-effect transistors (CHEMFETs) and ion-selective electrodes (ISEs) were developed based on this concept [44].

- According to the coordination chemistry, the complex formation between the redox-active host and phosphate ion involves a charge transfer process which can generate a current/potential perturbation response. This response can be measured as an amperometric/potentiometric signal whose intensity is correlated to the phosphate concentration [45].

- For some specific phosphate salts such as molybdophosphates, the electroluminescence phenomenon when binding with certain dyes such as rhodamine can be utilized for phosphate detection [46].

- Under a constant applied potential, the phosphate adsorption on a ITO (indium-tin oxide) electrode modulates the transmittance of the electrode. This optoelectrochemical response by measuring the transmitting light intensity was applied for phosphate concentration determination [47].

- During the oxidation process of glucose on a catalytic electrode, the presence of phosphate can result in a reduction of the catalytic current and the reduction magnitude is related to the phosphate concentration. This is applied as an indirect method for phosphate measurement [48].

- On the self-assembled monolayers of thiols modified gold electrode surface, the blocking kinetics in ferrocyanide electron transfer process induced by phosphate ions provides a pathway to measure the phosphate concentration [49].

- The voltammetric ion transfer process of phosphate ion facilitated by ionophore at two immiscible electrolyte interface can be utilized as a potentiometric detection method of phosphate [50].

- By modifying the electrode surface with phosphate sensitive enzymes, phosphate concentration can be determined based on the change of the electrode electrochemical properties [51].
With the presence of phosphate ions, the conductivity of certain chromogenic conductive polymers changes upon the increasing of phosphate concentration [52]. This can be utilized as a conductometric method for phosphate detection.

Considering the main technique, electroplating, used in this work, the developed method is focused on potentiometric metal sensors. Various species of metals [53-57] have been studied and used as sensing materials in the past. Among these efforts, an ISE based on cobalt (Co)/cobalt oxide (CoO) was demonstrated with some success in phosphate detection [58-60] in soil extraction [61], which indicates that a Co electrode can be applied for selective detection of phosphate in an aqueous solution. However, there still exist technical challenges such as complex fabrication processes, instability, and severe ion and oxygen interference for practical implementations.

Therefore, the objective in this work was developing a high-quality microsensor with a well-defined configuration based on in-situ electroplating of nanostructured cobalt, which is expected to have better performance such as faster response, increased stability and detection limit owing to the increased specific surface area. To achieve this, we proposed in-situ electroplating of a layer of Co-Cu alloy film on a micropatterned electrode surface and then obtained a nanostructured Co electrode through dealloying copper (Cu). Similar approaches using binary alloys have been studied to obtain nanoporous metal film synthesis for sensor applications [62]. The basic mechanism of the nanostructure is shown in Figure 4: a layer of binary alloy consisting of metals A and B is first synthesized on the substrate through a specified process route (e.g., thermal treatment [63] and co-electrodeposition [64]), then an agent [63] or electrochemical process [64] is chosen according to the chemical activity for selectively dealloying one metal component from the alloy layer. Therefore, the nanostructure after dealloying is directly dependent on the phase structure in the alloy.
Figure 4 The mechanism of nanostructure formation by selectively dealloying a binary alloy.

According to the Co-Cu binary alloy phase diagram [65], Co and Cu are completely miscible at low temperature, which makes pulsed electroplating (PEP) suitable for depositing the alloy in a wide concentration range. According to the research on the PEP process of Co-Cu [66], the microstructures of the alloy are closely related to the electroplating parameters, like electroplating bath constitution, current density, and duty cycle. In the electroplating bath solution, Cu$^{2+}$ and Co$^{2+}$ ions coexist so that during the pulse-on time, Co and Cu are deposited onto the substrate spontaneously. In addition to the depositing process, a displacement reaction between Cu ions and deposited Co during the pulse-off time also affects the content and morphology. Under both the effects of the electroplating process and displacement reaction, a Co-Cu alloy with a nanostructure is deposited onto the substrate. After dealloying the Cu portion, only nanostructured Co is left.

2.2 Fabrication

The sensor integration with a nanostructured Co electrode was achieved by a three-step fabrication process: photolithography, electroplating, and dealloying.
Figure 5 Sensor electrode layer fabrication process: (a) Au/Ti seed layer deposition; (b) photoresist patterning; (c) Co-Cu alloy electroplating; (d) photoresist stripping, (e)-(h) electrode patterning and (i) dealloying of Cu to form a nanofibrous electrode layer.

2.2.1 Photolithography
Starting from a 3-inch thermally oxidized silicon wafer, a Au/Ti thin film was deposited on the wafer surface as a seed layer (Figure 5 (a)). Microposit S1813 (Shipley Co.) photoresist (PR) was applied and spin-coated at 3,000 rpm for 30 s and baked at 105 °C for 180 s, subsequently. The substrate was exposed to UV (I-line) using an aligner (EVG 620) for 8 s with a soft-contact (~10 μm gap). The exposed substrate was then soaked in developer (MIF CD-26, Shipley Co.) for 40 s. After rinsing the substrate, photo-defined patterns were inspected under a microscope. Finally, the substrate was hard-baked at 105 °C for 10 min (Figure 5 (b)). A similar photolithography process was applied for electrode contact patterning (Figure 5 (e)-(h)).
2.2.2 Electroplating and Dealloying
As shown in Figure 5 (c), electroplating of Co-Cu alloy was conducted within an exposed area patterned by photolithography. The current density was set as 75 mA/cm² and duty cycle as 0.2 (ton=2ms). The bath solution consisted of 0.7 M CoSO₄·7H₂O, 0.025 M CuSO₄·5H₂O, 0.18 M Na₃C₆H₅O₇·2H₂O, and 1/50 part of saccharin. Citrate was used as a complexing agent to plate a smooth deposit through leveling action. Saccharin was used as a wetting agent so that hydrogen bubbles produced during plating did not stick to the substrate surface, eliminating the formation of pits. After electroplating for 10 min, a layer of alloy approximately 1.7 µm thick was deposited. The PR was then 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 CuSO₄·5H₂O + 100 ml of NH₄OH) was used to dealloy Cu in the alloy so that only nanofibrous cobalt was left.

2.3 Test
2.3.1 Composition and Morphology
To characterize the fabrication process and sensor performance, sensor electrodes before selective etching as well as after selective etching and a pure cobalt electrode were prepared. Surface compositions and morphologies were analyzed using energy dispersive spectrometry (EDS) and scanning electron microscopy (SEM).

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

2.3.2 Phosphate Sensing
The phosphate sensor electrodes were tested with standard KH₂PO₄ solutions with concentrations ranging from 10⁻³ M to 10⁻² M at room temperature (23 °C). The pH was adjusted to 7.5 using potassium hydroxide (KOH) and hydrogen chloride (HCl).
The fabricated phosphate sensor chip was connected with a reference electrode (Ag/AgCl). Before testing, the sensor chips were immersed in deionized (DI) water as pretreatment for approximately 24 h to form a cobalt oxide (CoO) layer on the electrode surface. Both electrodes were then immersed in the $10^{-4}$ M phosphate standard solution under stirring condition until a steady potential was achieved. Figure 6 shows the experimental setup for polarization and calibration. The potential between the sensor and reference electrode was monitored by a multimeter (UNISENSE).
2.4 Results and Discussion

2.4.1 Fabrication Results

Figure 7 (a) Schematic view (before and after packaging) and (b) real view of the fabricated sensor chip.

As Figure 7 (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 (Figure 7 (b)), 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 insulation from a test solution.
Figure 8 shows the EDS analysis result, which presents the Cu composition on the sensor electrode surface before and after the dealloying process.

![Figure 8 Cu composition comparison on the electrode surface: before (a) and after (b) dealloying process.](image)

The amount of Cu in the alloy decreased after the electrode was dealloyed for some time as expected. To increase the surface area, Cu must be dealloyed from the alloy. However, an excessive dealloying time caused the electrode to peel from the substrate. Based on this observation, the proper dealloying time was set at approximately 10 s.
Figure 9 Surface morphology of nanofibrous Co electrode. (a) before etching and (b) after etching.

The electrodes fabricated with 75 mA/cm² current density and 10 s dealloying time were observed with SEM to obtain details about the surface morphology. In Figure 9, two electrodes were fabricated with 75 mA/cm² current density in the same bath solution. SEM images showed clearly that the electrode before dealloying has a smooth surface. After the dealloying process, the Co sensing surface area increased with increasingly nanofibrous textures. During the electroplating process, Co and Cu were co-electroplated to form the alloy with a smooth surface, and the selective etching successfully removed Cu from the alloy, leaving behind Co with nanofibrous textures.

2.4.2 Sensor Functions
To characterize the working range of the developed sensor, we prepared KH₂PO₄ solutions with concentrations ranging from 10⁻⁵ M to 10⁻² M. The nanofibrous Co electrode was used as a working electrode. According to the theory of electrochemistry, the potential (mV) measured on the electrode is governed by the Nernst equation [59]:

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

$$E_{\text{cell}} = E^0 + \frac{0.5916V}{n} \log_{10}(K_{\text{eq}})$$  \hspace{1cm} (2)

where the potential is decided by the reaction quotient $K_{\text{eq}}$.

When the Co sensor electrode is immersed in DI water, the baseline potential is developed based on

$$K_{\text{eq}} = \frac{[\text{CoO}]^2}{[\text{Co}]^2[O_2]}$$  \hspace{1cm} (3)

When phosphate is present in the water, it will combine with CoO, and a new balance will be reached. The reaction quotient for the new equilibrium is

$$K_{\text{eq}} = \frac{[\text{OH}^-][\text{Co}(\text{PO}_4)_2]^2}{[\text{Co}]^2[O_2]^2[H_2\text{PO}_4]^2}$$  \hspace{1cm} (4)

At a fixed stirring speed and pH, every factor except the concentration of $H_2\text{PO}_4^-$ can be considered as constant, so we can expect a shifted potential in the form of

$$E = E^0 + m\log([a])$$  \hspace{1cm} (5)

where $m$ is the slope and $a$ is the activity of the measured ion species. For estimation, the solution is assumed as an ideal solution and the activity directly reflects the concentration. Therefore, we expect a linear relation between electrode potential and $\log[KH_2\text{PO}_4]$.

Figure 10 shows measured potential as a function of logarithm of phosphate concentration. The test result shows that this nanofibrous electrode performed as the Nernst equation describes.
**Figure 10** Sensor responses as a function of logarithm of phosphate concentration and signal shifting after being used several times.

The sensing mechanism (Figure 11) proposed by Xiao et al. is based on the formation of the nonstoichiometric compound Co$_{1.5}$O formation on the Co surface [57]. It is assumed that the Co$^{2+}$ (□) cavities in the Co$_{1.5}$O layer, serving as the host, has a preference to accept H$_2$PO$_4^-$ as guest. This is considered as the key process in the sensor’s response to phosphate ions.
Figure 11 $\text{Co}_{\delta\text{O}}$ structure. The charge balance is achieved by replacing $\text{Co}^{2+}$ (□) by two $\text{Co}^{3+}$ in its neighborhood.

The nonstoichiometric oxide of $\text{Co}_{\delta\text{O}}$ can also have a potentiometric response to the $\text{O}_2$ partial pressure, which is considered as interference to phosphate sensing. The mechanism of the oxygen interference was considered as (1) the adsorption of an oxygen atom at the surface, (2) two of the nearby $\text{Co}^{2+}$ being oxidized to $\text{Co}^{3+}$ while the oxygen atom being reduced to $\text{O}^2-$, and (3) $\text{Co}^{2+}$ diffusing from the inner to the surface, leaving a hole (□). This proposed a mechanism for the oxygen interference on the Co potentiometric sensor and pointed out the key role of CoO membrane in phosphate sensing.

Based on Xiao et al.’s work, Ravi K. et al. proposed a “mix potential response” mechanism to discuss and describe the effect of pH and dissolved oxygen on the Co electrode response [67]. The phosphate sensing mechanism is postulated to be a two-step process: 1) the formation of oxide film, which can be presented with two half-cell reactions (Equations (6) and (7)) and 2) the reaction between phosphate and the cobalt oxide (Equations (8), (9), or (10) depending on the pH of the solution):

\[
2\text{Co} + 2\text{H}_2\text{O} \leftrightarrow 2\text{CoO} + 4\text{H}^+ + 4\text{e}^- \quad (6)
\]

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O} \quad (7)
\]
When the sensor is immersed in the solution containing phosphate, cobalt phosphate is formed on the electrode surface:

\[
3\text{CoO} + 2\text{H}_2\text{PO}_4^- + 2\text{H}^+ \leftrightarrow \text{Co}_3(\text{PO}_4)_2 + 3\text{H}_2\text{O} \quad \text{(at pH 4.0)} \quad (8)
\]

\[
3\text{CoO} + 2\text{H}_2\text{PO}_4^2+ + \text{H}_2\text{O} \leftrightarrow \text{Co}_3(\text{PO}_4)_2 + 4\text{OH}^- \quad \text{(at pH 8.0)} \quad (9)
\]

\[
3\text{CoO} + 2\text{PO}_4^3- + 3\text{H}_2\text{O} \leftrightarrow \text{Co}_3(\text{PO}_4)_2 + 6\text{OH}^- \quad \text{(at pH 11.0)} \quad (10)
\]

These reactions give a potential output related to the logarithm of the phosphate concentration based on the description of the Nernst equation. Therefore, according to the proposed mechanism, the potentiometric response of phosphate ions and the oxygen interference are highly dependent on the sample pH value and the oxygen concentration determined by the stirring rate. The mechanism previously proposed by Xiao et al. failed to explain such behavior.

Ravi K. et al.’s work describes the notion that Co electrodes respond to different phosphate species under different pH. However, this proposed mechanism has several limitations: 1) this mechanism ignored that all phosphate species co-existed with different ratios in solutions with different pH. Therefore, the electrode was not responding to a single species but all of them, which is a mixed response in reality; 2) in the proposed mechanism reactions, the ratio of CoO to phosphate is constant at 3:2, which indicates a constant EMF sensitivity: \(~20\, \text{mV/decade.}\) However, the observed phenomenon is \(~60\, \text{mV/decade at pH 4.0, \sim 40 mV/decade at pH 7.5 and \sim 20 mV/decade at pH 12.}\) Therefore, the actual mixed potential response mechanism is more complex; the Co electrode has different sensitivities to different phosphate species. This is discussed and analyzed in this dissertation work.

To understand the electrochemical behavior of a Co electrode in aqueous solution, we must determine details about the reaction processes. Because Co electrode pretreatment in water to form a CoO layer is a key process, we start from the Co behavior in water [68].
Figure 12 presents the E–pH diagram for Co at a soluble compound concentration of $10^{-1.0}$ M. No complexing agents other than OH$^-$ or HOH and no species that would produce insoluble compounds are present [69].

![E–pH diagram for Co species. Soluble species concentrations (except H$^+$) =10$^{-1.0}$ M. Soluble species and most solids are hydrate. No agents producing complexes or insoluble compounds are present other than HOH and OH$^-$ [69].](image)

From this diagram, we can state that the electrochemical behavior of cobalt in aqueous solutions is determined by the composition and pH value. By connecting a Co electrode to a Ag/AgCl reference electrode, the Co electrode behavior was studied by the potential signal. The open-circuit potential of cobalt
electrodes was recorded in aqueous solutions covering the pH range of 1–13 [68]. The results reveal that the electrochemical behavior of cobalt in alkaline solutions is different from that in acidic or neutral solutions. In acidic solutions (pH 1–6), the open-circuit potential is a constant value depended on the solution pH and becomes more negative as pH increases. In neutral solutions (pH 7), the open-circuit potential reaches its steady state in less than 15 min. In basic solutions (pH 13), the open-circuit potential shows two arrests. The first occurs at a steady value of approximately -800 mV, which extends over 70 min and jumps to the second arrest that occurs at a more positive steady value and extends over more than 5 h. The results show clearly that the cobalt electrode undergoes a steady corrosion process in acidic solutions and there is a linear relation between the electrode potential and the solution pH [68]. Such a linear function can be represented as

$$E_{\text{SS}} = a - b \times \text{pH}$$  \hspace{1cm} (11)

where $a$ is the steady-state potential at pH 0 and $b$ is the slope of the linear relationship. The value of $a$ was found to be equal to -240 mV. The slope of the linear relation is equal to -33 mV per pH unit. According to the E–pH diagram, a value of approximately -30 mV/decade for slope $b$ suggests that the corrosion process of Co in acidic solutions up to pH 6 is an electrochemical process that can be represented by

$$\text{Co} \rightarrow \text{Co}^{2+} + 2e^-$$  \hspace{1cm} (12)

Researchers also performed X-ray photoelectron survey (XPS) spectra and depth profiling to study the Co electrode behavior. A mechanism for the pretreatment of a Co electrode in aqueous solution under different pH was proposed.

According to the E–pH diagram, the presence and thickening of the passive film, occurring in neutral or basic solutions, which are confirmed by XPS, can be attributed to the formation of a duplex film on the electrode surface according to different mechanisms:

$$\text{Co} + \text{H}_2\text{O} \rightarrow \text{Co(H}_2\text{O)}_{\text{ads}}$$  \hspace{1cm} (13)
\[ \text{Co(H}_2\text{O)} \rightarrow \text{Co(OH)}^++\text{H}^++2\text{e}^- \]  
\[ (14) \]

The sequence of the reactions depends on the pH of the solution:

In acidic solutions,

\[ \text{Co(OH)}^++\text{H}^+ \rightarrow \text{Co}^{2+}+\text{H}_2\text{O} \]  
\[ (15) \]

and continuous dissolution of cobalt or its passive film occurs, which leads to the high rate corrosion of Co.

In neutral solutions,

\[ \text{Co(OH)}^++\text{H}_2\text{O} \rightarrow \text{Co(OH)}_2+ \text{H}^+ \]  
\[ (16) \]

\[ \text{Co(OH)}_2 \rightarrow \text{CoO}+\text{H}_2\text{O} \]  
\[ (17) \]

In this case, the passive film is stabilized, and a relative smaller rate of corrosion of the cobalt is recorded.

In alkaline solutions,

\[ \text{Co(OH)}^++\text{OH}^- \rightarrow \text{Co(OH)}_2 \]  
\[ (18) \]

\[ \text{Co(OH)}_2+\text{OH}^- \rightarrow \text{CoOOH}+\text{H}_2\text{O}+2\text{e}^- \]  
\[ (19) \]

\[ 3\text{CoO}+2\text{OH}^- \rightarrow \text{Co}_3\text{O}_4+\text{H}_2\text{O}+2\text{e}^- \]  
\[ (20) \]

The formation of either CoOOH or Co$_3$O$_4$ stabilizes of the passive film and generates another layer on top of the original CoO passive film. The formation of Co(OH)$_2$ on the cobalt surface in basic solutions was confirmed by Bewick et al. by *in-situ* infrared (IR) spectroscopic investigations of the passive oxide film on cobalt. These authors have identified peaks corresponding to the oxidation of Co(OH)$_2$ into Co(III). This explains the change in the characteristics of the passive film recorded by the electrochemical experiments and the XPS measurements in basic solutions.

Therefore, the recommended pretreatment of a Co electrode to obtain CoO film is neutral condition. After the pretreatment process is complete, the Co electrode is applied for phosphate sensing under different pH to characterize electrode performance.
According to Equation (12), the potential signal arises from the oxidation of Co into Co$^{2+}$. The presence of H$^+$ and phosphate shift the oxidation process that changes the potential signal, which indicates the concentration of H$^+$ and phosphate.

In contrast to the mechanism proposed in Equations (6)–(10), we propose another mechanism based on Xiao et al.’s mechanism that the CoO film serves as a “solid electrolyte” consisting of Co$^{2+}$ and O$^{2-}$ ions that maintains a steady concentration zone of Co$^{3+}$ and O$^{2-}$ (Figure 13). Ions in solution diffuse into CoO film affecting the concentration of Co$^{2+}$ and O$^{2-}$ to yield the potential signal. Without a CoO film on the surface, the Co$^{2+}$ ion concentration will be easily affected by solution conditions such that a stable signal cannot be achieved.

![Figure 13 CoO film on the electrode surface.](image-url)
However, the difference in the electrode’s sensitivity under various pH is not explained. According to Equation (11), we expect that the response curve of phosphate concentration is shifted without changing the slope (sensitivity). However, in the actual experiment, both the intercept and slope of the curve are shifted. According to the “mixed potential response” mentioned before, we can assume that the Co electrode has different sensitivity to different phosphate species and the concentration distribution of phosphate species under different pH conditions is different. The final potential response is a weighted function of the sensitivities of all phosphate species.

For phosphate, $K_{a1} = 7.11 \times 10^{-3}$, $K_{a2} = 6.28 \times 10^{-8}$, $K_{a3} = 4.5 \times 10^{-13}$. By using pure KH$_2$PO$_4$ to prepare phosphate solutions, the fractions of different phosphate species (H$_2$PO$_4^-$, HPO$_4^{2-}$ and PO$_4^{3-}$) under various pH are shown in Figure 14.

![Figure 14 Distribution of phosphate species in varying pH conditions.](image)
We can see that below pH 12, the concentration of $\text{PO}_4^{3-}$ is negligible. Therefore, $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$ are the main contributing species to the potential response. Here, we propose the responding mechanism in the CoO “solid electrolyte” film as

\[
\begin{align*}
\text{Co}^{2+} + 2\text{H}_2\text{PO}_4^- &\rightarrow \text{Co}[(\text{H}_2\text{PO}_4)_2] \quad (21) \\
\text{Co}^{2+} + \text{HPO}_4^{2-} &\rightarrow \text{Co}[(\text{HPO}_4)] \quad (22) \\
3\text{Co}^{2+} + 2\text{PO}_4^{3-} &\rightarrow \text{Co}_3[(\text{PO}_4)_2] \quad (23)
\end{align*}
\]

where the phosphate ions fall into oxygen cavities in CoO film and are subject to a charge balance. According to the Nernst equation, Equation (21) has sensitivity of ~60 mV/decade to $\text{H}_2\text{PO}_4^-$, Equation (22) has ~30 mV/decade to $\text{HPO}_4^{2-}$, and Equation (23) has ~20 mV/decade to $\text{PO}_4^{3-}$. Combining the weighted function of mixed potential response, we obtain

\[
\text{Sensitivity} = 60 \times (\% \text{H}_2\text{PO}_4^-) + 30 \times (\% \text{HPO}_4^{2-}) + 20 \times (\% \text{PO}_4^{3-}) \text{[mV/decade]} 
\quad (24)
\]

According Equation (24), the sensitivity–pH diagram is plotted in Figure 15, which is consistent with the current experimental results.
Figure 15 Sensitivity–pH diagram.

It is hypothesized that even by adding pure KH$_2$PO$_4$ only, the percentage of phosphate species and electrode sensitivities are greatly influenced by various pH conditions. In Figure 15, there are two “plateau” regions in which the Co electrode has a good resistance to pH fluctuations. However, for actual application of a sensor in a natural water body whose pH value falls within 6–8, special attention to the water pH value must be paid. Small fluctuation of the pH value will have a large impact on the electrode’s sensitivity, which limits the repeatability of phosphate sensors.
CHAPTER THREE: NANOPOROUS CO-CU ELECTRODES FABRICATED BY POROUS TEMPLATE-BASED ELECTROPLATING (PORTE)

3.1 Introduction
In previous work, nanofibrous Co electrodes were fabricated by PEP of Cu-Co alloy and selective dealloying of Cu for phosphate sensing. However, this revealed that potentiometric Co electrodes suffer from pH fluctuations and oxygen interference, which limits its applications in real environment. Alloying another metal element inert to phosphate could stabilize the sensor electrode by affecting the redox reaction and reducing the overactivity of Co [70]. However, oxygen interference still exists in potentiometric measurements; here, we seek to employ an amperometric sensor by shifting the electrode surface redox reaction to eliminate oxygen interference. We designed and fabricated a textured amperometric Co-Cu microelectrode using PEP with a sacrificial glass fiber paper template and characterized the sensor for in situ phosphate monitoring.

3.2 Fabrication
3.2.1 Photolithography
As shown in Figure 16, starting from a 3-inch wet thermally oxidized silicon wafer, a Au/Ti thin film was deposited by thermal evaporation as a seed layer. Microposit S1813 (Shipley Co.) photoresist (PR) was then applied and spin-coated at 3,000 rpm for 30 s and baked at 105 °C for 180 s. After the substrate was exposed to UV (I-line) using an aligner (EVG 620) for 8 s with a soft-contact mode, the exposed substrate was processed in a developer (MIF CD-26, Shipley Co.) for 40 s. After rinsing the substrate, photo-defined patterns were inspected under a microscope. The substrate was then hard-baked at 105 °C for 10 min. Finally, the wafer was immersed in Au and Ti etchant for electrode patterning. The finished 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.
3.2.2 Pulsed Electroplating

Fibrous glass filter paper (Fisherbrand, 09-804-142H) was attached to the patterned Au electrode surface and fixed by two glass plates (Figure 17 (a), (b)). As depicted in Figure 17 (c), one end of glass fiber paper was dipped in electrolyte consisting of 0.7 M CoSO$_4$·7H$_2$O, 0.025 M CuSO$_4$·5H$_2$O. While the paper was entirely soaked, a pulsed potential was applied with a pulsed power supply (DUPR 10-1-3, Dynatronix) (Figure 17 (d)). The constant potential was set as 1.3 V with a duty cycle of 0.5 ($t_{on}$=5 ms). After electroplating for 6 h, the layer of Cu-Co alloy was deposited into the glass fiber filter paper. Finally, the electrode was immersed into buffered oxide etchant (BOE) for 5 min to thoroughly remove glass fiber so that the nonporous electrode could be exposed.

**Figure 16 Photolithography process.**
3.3 Test

3.3.1 Composition and Morphology
Textured and planar electrodes were prepared as a reference working electrodes for comparative study. Electrode compositions and morphologies were characterized using EDS and SEM.

3.3.2 Phosphate Sensing
The developed phosphate sensor electrodes were characterized using standard \( \text{KH}_2\text{PO}_4 \) solutions ranging from \( 10^{-2} \) to \( 10^{-6} \) M at 23 °C. Twenty-five millimolar potassium hydrogen phthalate (KHP) was used as a buffer solution at pH 4.0.

As a pretreatment, the newly fabricated phosphate sensor chips were immersed into DI water for 24 h to form a CoO layer on the electrode surface. The sensor chips were then connected with a Ag/AgCl reference electrode (Microelectrodes Inc.) and placed in a \( 10^{-4} \) M phosphate standard solution under stirred condition.

Figure 17 Co-Cu electrode electroplating process with glass fiber filter paper as sacrificial template [71].
until a stable potential was achieved. The same experimental setup shown in Figure 6 was applied for polarization and calibration. The potential or current between the two electrodes was monitored by a multimeter (UNISENSE A/S).

3.4 Results and Discussion

3.4.1 Sensor Fabrication
The EDS analysis showed that the electrode consists of Cu-Co (rich) alloy (Figure 18).

Here, Cu was applied to stabilize the sensor electrode by affecting the redox reaction and reducing the overactivity of Co. Although the Cu content was relatively low, the amount of Cu, as a phosphate inert element, may be independent on phosphate measurements. As shown in Figure 18, the Co-Cu alloy electrode showed a Co-rich composition, expecting high sensitivity toward phosphate ions.

![EDS test results for the electrode composition of the developed phosphate sensor before pretreatment](image)

Figure 18 EDS test results for the electrode composition of the developed phosphate sensor before pretreatment [71].

During the electroplating process, Co and Cu were co-electroplated to form the Co-Cu alloy. The SEM image (Figure 19 (a)) shows that a smoother surface was obtained without the glass fiber template. It appears that the small particles on the surface resulted from the formation of oxides. On the other hand, an electrode film with rough surface and nanopores and trenches was obtained from the fabrication process where glass filter paper was applied as template (Figure 19 (b), (c)). Compared with the smooth surface,
the nanoporous structure increased the sensor electrode’s specific surface area, which provides more reaction sites for detection of low-concentration phosphate.

Figure 19 Co-Cu electrodes: (a) surface morphology without template and (b), (c) surface morphology and cross section view after selective etching of glass fiber template.
3.4.2 Sensor Functions and Phosphate Detection
In potentiometric tests, the Co-Cu electrode fabricated with glass fiber as template responded immediately (< 30 s) when phosphate was present with a sensitivity of 34 mV/decade. Figure 20 shows measured potentials as a function of the logarithm of phosphate concentration. The calibration curve shows that this nanofibrous electrode performed linearly as the Nernst equation describes. As a control sample, the planar Co-Cu sensor electrode fabricated without template was also tested. It was demonstrated that the nanoporous surface improved the working range of the sensor as well as its detection limit.

![Figure 20 Sensor responses as a function of phosphate concentration [71].](image)
However, dissolved oxygen (O$_2$) in solution will shift the potentiometric response to phosphate, as indicated by Equation (9), which can lead to inaccurate detection and requires oxygen measurements for additional interpretation. Therefore, the sensor operation mode was changed to amperometry to investigate the effect of shifting the electrode surface redox reaction on eliminating oxygen interference.

CV tests were conducted in solutions with different concentrations of phosphate and oxygen-saturated and deoxygenated 10$^2$ M phosphate solutions. The CV results show an obvious reduction peak at -1.1 V and an oxidation peak at -0.3 V with different peak currents according to phosphate concentration (Figure 21(a)). In addition, the CV curves show that applied potentials below -300 mV vs. Ag/AgCl experience oxygen interference, whereas applied potentials above -300 mV have no oxygen interference (Figure 21(b)). The chloride (Cl$^-$) and sulfate (SO$_4^{2-}$) ion interferences of the fabricated sensor electrode were characterized by a CV test as shown in Figure 22. As discussed in the previous chapter, the phosphate sensing behavior arises from oxidation of Co; therefore, the calibration curves were created and compared at applied potentials above -300 mV, and the amperometric signals at -250 mV were found to have a good linear response to different phosphate concentrations with stable sensitivity and suppression of oxygen interference (Figure 23).
Figure 21 CV tests under different phosphate concentrations (a) and air saturated and deoxygenated conditions (b) [71].

Figure 22 Characterization of (a) Cl⁻ and (b)SO₄²⁻ ion interferences of fabricated sensor electrode.
The electrochemical reactions on the Co electrode surface are complex and involve several ion species, contributing to overall signals. To simplify the calculation process, only key reactions are discussed here.

For the potentiometric method, a working (sensing) electrode and a reference electrode are connected to form a cell, and open-circuit potential is measured; that is, no external potential is applied to the sensor electrode, and no current flows in the cell after equilibrium is achieved on the electrode surface. However, under this condition, some interference reactions also occur on the electrode surface.
In contrast to the potentiometric method, an external potential is applied between the sensor and reference electrode, by which the electron energy on the sensor electrode is adjusted so that some surface reactions can be promoted or depressed according to the application requirements.

In the case of the Co electrode, the reduction of oxygen on the electrode surface is treated as interference that must be depressed, but the oxidation of Co into Co\(^{2+}\) should be promoted. The two reactions are shown as

\[
\begin{align*}
\text{Co} & \leftrightarrow \text{Co}^{2+} + 2e^- \quad (25) \\
\text{O}_2 + 4e^- & \leftrightarrow 2\text{O}^{2-} \quad (26)
\end{align*}
\]

Reaction (25) is the key process that affects the concentration of Co\(^{2+}\) on the electrode surface for phosphate sensing.

To simply the discussion, we start from an ideal situation in which oxygen is totally depleted in solution so that only the phosphate species react with the sensor electrode. In the CV curve, a reduction peak around -1.1 V is observed, which means that beyond -1.1 V, the reduction current of Co\(^{2+}\) is negligible. Therefore, the total current arises from the oxidation process of Co, which can be described by the Butler–Volmer equation [72]:

\[
i = F A k^0 [C_0(0, t)e^{-a f(E-E^0)} - C_R(0, t)e^{(1-a) f(E-E^0)}]
\]

(27)

where \(a, n, F, A, k^0, R, \) and \(T\) represent the transfer coefficient, number of electrons, Faraday constant, area of the electrode, rate constant, gas constant, and temperature, respectively. \(E\) is the potential applied between the sensor and reference electrode. \(E^0\) represents the open-circuit potential between the sensor and reference electrode when the reaction is in equilibrium.

As discussed, the reduction current is negligible, so the second term in Equation (27) can be approximated as 0. The current response can then be described as

\[
i = F A k^0 C_0(0, t)e^{-a f(E-E^0)}
\]

(28)
In this situation, $a$, $n$, $F$, $A$, $k^0$, $R$, and $T$ are constant. In addition, when the reduction current is very small ($E>-1.1 \text{ V}$), the reduction process of $\text{Co}^{2+}$ can be neglected so that the $C_0(0, t)$ can be considered as constant for simplification. Hence, the response to the phosphate concentration is reflected only by the shifting of overpotential ($E-E^0$).

If the overpotential applied between the electrodes is sufficiently small, the Butler–Volmer equation is simplified into a linearized form (for large overpotential, Butler–Volmer is simplified to a Tafel response). The linearized Butler–Volmer equation is

$$i = FAk^0C_0(0, t)e^{-af(E-E^0)} \approx C^*(E-E^0)$$

where $C^*$ is the product of all constants.

As discussed previously in the Nernst equation, we have $E^0$ as

$$E^0 = E^* + K\log[H_2\text{PO}_4^-]$$

Substituting Equation (30) into Equation (29), we have

$$i = C^*\{(E-E^*)-K\log[H_2\text{PO}_4^-]\}$$

which indicates that in the small overpotential range, the amperometric response of the Co electrode is linear to $\log[H_2\text{PO}_4^-]$.

We can now consider the oxygen reduction current. According to the Butler–Volmer equation,

$$i = FAk^0[C_{\text{Co}}(0, t)e^{-af[\text{Co}]}e^{[E-E(\text{Co})]}-C_{\text{O}_2}(0, t)e^{[1-a\text{[O}_2]]}[E-E(\text{O}_2)]]$$

We can see that the second term represents the oxygen reduction current based on Reaction (26). Again, the CV test is applied to determine the region in which the second term is neglectable so that oxygen interference is depressed.

In summary, the target overpotential region can be found in the overlapped area in which the Co electrode’s small overpotential region and the depressed oxygen reduction region coexist. In this region, a linear current
response to phosphate concentration with depressed oxygen interference can be expected, which is in good agreement with the experimental results.
CHAPTER FOUR: ZNO NANOFILAKES AS TEMPLATE FOR IN-SITU ELECTRODEPOSITION OF NANOSTRUCTURED COBALT ELECTRODE FOR AMPEROMETRIC PHOSPHATE SENSOR

4.1 Introduction
Based on the previous research results, we further explored and improved the Co-based phosphate sensor electrode performance with another strategy to introduce nanostructures. Inspired by the electroplating metal nanowires with AAO template, this work seeks to develop a novel fabrication process with in-situ hydrothermal grown ZnO nanoflake as a template to synthesize nanostructured cobalt electrodes for phosphate detection. Compared with AAO template, in-situ grown ZnO nanoflakes as template simplify the fabrication process. AAO template usually must be attached to a substrate surface with fixtures and also requires a high-pressure and -temperature experimental condition. In addition, applying the AAO template is limited by electrolyte viscosity and dissociation of water during electroplating, which leads to blockage of pores in AAO and causes defects in deposited metal nanowires [73].

From the improved reaction site and adsorption efficiency with increased specific surface area, it is expected that a nanostructured cobalt electrode will have better performance compared with a bulk cobalt electrode. In this work, we designed and fabricated a nanostructured cobalt microelectrode by electroplating with a sacrificial ZnO nanoflake template. According to the results in [18], ZnO nanoflakes can be synthesized by a hydrothermal method on a large area substrate in-situ and seedlessly, which was applied as a pretreatment process to form the nanoflake template. After the cobalt (Co) electroplating, the ZnO nanoflake template can be simply removed by diluted acid etching. With the fabricated electrode, we employed an amperometric method to characterize the effects of the nanostructure on the sensor performance.

4.2 Fabrication
As shown in Figure 24, the fabrication process is relatively simple with four steps: hydrothermal growth of the ZnO nanoflake template, photolithography, electroplating, and template etching.
4.2.1 Hydrothermal Growth of ZnO Nanoflakes
The hydrothermal growth of ZnO nanoflakes is following the process and parameters in [18]. First, 0.52 g of ZnSO$_4$·7H$_2$O (Fisher Scientific, Fair Lawn, NJ) was first dissolved in 90 ml of DI water (20 mM Zn$^{2+}$). Then, 3 ml of ammonia solution (28–30 wt. %) was added and stirred until all white sediment was dissolved. A thermally oxidized silicon wafer with a Au/Ti thin film deposited was soaked into the prepared solution, and the beaker was placed on a hotplate at 100 °C for 5 h. The wafer was then cleaned by DI water and dried by a nitrogen gun (Figure 24 (a)–(b)).

4.2.2 Photolithography
With the ZnO nanoflake modified wafer, Microposit S1813 (Shipley Co.) photoresist (PR) was applied on the wafer, which was then spin-coated at 3,000 rpm for 30 s and baked at 105 °C for 180 s, subsequently. The wafer was exposed to UV (I-line) using an aligner (EVG 620) for 8 s with a soft-contact (~10 μm gap). The exposed wafer was then developed in a developer (MIF CD-26, Shipley Co.) for 35 s. After rinsing the
substrate, photo-defined patterns were inspected under a microscope. Finally, the substrate was hard-baked at 105 °C for 10 min (Figure 24 (c)).

4.2.3 Electroplating, ZnO Etching, and Electrode Patterning
The patterned wafer was used as the cathode with a Pt mesh as the anode. Both electrodes were soaked into 75 mM CoSO₄ (Fisher Scientific, Fair Lawn, NJ), electrolyte and a current (i = 40 mA/cm²) was applied between them for 300 s for cobalt film electroplating. Because ZnO can be easily etched away by acid (10 wt % HCl), no additive or acid was added into electrolyte to remain neutral and protect the ZnO nanoflake template (Figure 24 (d)).

After the cobalt film electroplating, the PR pattern was stripped away by acetone, and the wafer was washed by diluted acid (10 wt. % HCl) for 3 s to remove the ZnO nanoflake template. The wafer was then washed by DI water and dried by a nitrogen gun (Figure 24 (e)–(f)).

Finally, after another photolithography process was carried out for electrode patterning, the patterned wafer was diced into individual sensor microelectrodes for characterization (Figure 24 (g)–(i)).

4.3 Characterization
4.3.1 Cobalt Film Characterization
To characterize the fabrication process and sensor performance, sensor electrodes before and after ZnO nanoflake template etching and a planar cobalt electrode were prepared. Surface compositions and morphologies were analyzed using EDS and SEM.

4.3.2 Phosphate Sensing
The phosphate sensor microelectrodes were tested with standard KH₂PO₄ solutions (Fisher Scientific, Fair Lawn, NJ) with concentrations ranging from 10⁻³ M to 10⁻⁶ M at room temperature (23 °C). The pH was stabilized at 4.0 using 25 mM potassium hydrogen phthalate (KHP) buffer solution (Fisher Scientific, Fair Lawn, NJ).
A phosphate sensor microelectrode was connected with a Pt mesh as a counter electrode and a Ag/AgCl milli-electrode (MI-401, Microelectrodes Inc.) as a reference electrode to build up a three-electrode system. Before testing, the sensor microelectrode was conditioned in DI water for approximately 24 h to form a CoO (cobalt oxide) layer on the electrode surface. All three electrodes were then immersed into the $10^{-4}$ M phosphate standard solution under the stirring condition for 30 min.

4.4 Results and Discussion

4.4.1 Sensor Surface Characterization

The element species and composition (atom. %) on the sensor electrode surface before and after ZnO nanoflake template etching are shown in Figure 25.

**Figure 25** Electrode surface composition comparison: before (a) and after (b) selective etching process [74].

The EDS analysis results with peak height and atomic weight (%) of each element showed that the zinc was completely etched off and the amount of oxygen was significantly reduced, indicating that etching in diluted acid for 3 s effectively removed the ZnO template from the electrode surface without affecting the cobalt composition. Etching over a longer time (30 s) removed the cobalt film, showing that 3 s of etching time is optimal for selective etching.
After confirming the electrode composition using EDS, SEM characterization of the planar cobalt electrode, ZnO nanoflake template, and cobalt electrode before and after the etching template was carried out to observe the electrode surface morphologies and to validate the idea of using a ZnO nanoflake template to involve the nanostructure into the cobalt electrode.

![Figure 26 Surface morphology of electrode surface electroplated with 40 mA/cm²: (a) planar cobalt, (b) hydrothermal grown ZnO nanoflake template, (c) before and (d) after selective etching of ZnO nanoflake template [74].](image)
As shown in Figure 26 (a) and (d), both planar and nanostructured cobalt electrodes were electroplated with the same current density (40 mA/cm²) and bath solution. However, they showed different morphologies owing to the ZnO nanoflake template. By comparing Figure 26 (b) and (c), it was observed that the ZnO nanoflake template was covered by a layer of cobalt film while maintaining the nanostructures. In addition, during the electroplating process, the ZnO nanoflake template reduced the surface tension of the electrolyte on the electrode surface; therefore, a low-residue stress cobalt film was electroplated without adding extra agents and additive. The electroplated cobalt film showed good adhesion on the substrate compared to a directly plated film, which may be easily peeled off due to residue stress in film. Figure 26 (c) and (d) clearly demonstrated that after selective etching of ZnO nanoflake template, porous structures were formed within the space around nanoflakes, which further enhance the specific surface area of the electrode.

4.4.2 Sensor Performance Characterization
The fabricated sensor performance was characterized by cyclic voltammetry (CV) tests with a scan rate of 50 mV/s from -1.0 V towards positive with different phosphate concentrations. Figure 27 shows the CV test results for both planar and nanostructured cobalt electrodes. The planar and nanostructured cobalt electrodes showed different electrochemistry responses to phosphate (KH₂PO₄). From the CV curve, a constant potential (-0.2 V vs. Ag/AgCl) was chosen to read out the corresponding current response. Figure 28 (a) shows that the planar electrode’s response (µA) increased with increasing phosphate concentration, whereas the nanostructured electrode showed a reversed trend with a noticeable oxidation peak around -0.4 V vs. Ag/AgCl when the phosphate concentration was above 10⁻⁵ M (Figure 28 (b)). No oxidation peak was observed in the CV test with the planar electrode.
Figure 27 CV tests under different phosphate concentrations with (a) planar Co electrode and (b) nanostructured Co electrode under pH 4.0 (25 mM KHP buffer) condition [74].

Figure 28 Sensor response as a function of phosphate concentration with (a) planar Co electrode and (b) nanostructured Co electrode under pH 4.0 (25 mM KHP buffer) condition [74].

The nanostructured cobalt electrode showed a linear current response at -0.2 V vs. Ag/AgCl with a smaller deviation error than the planar electrode. The planar electrode showed greater sensitivity (-33.48 μA/decade) in the concentration range of $10^{-5}$ to $10^{-3}$ M than the nanostructured electrode, which showed less sensitivity (13.17 μA/decade) with increased concentration range of $10^{-6}$ to $10^{-3}$ M. This result validates that the nanostructure enhanced the sensor’s LOD by providing more reaction sites. The difference in response and
sensitivity can be explained by the proposed hypothesis that the dominant reaction kinetics become different depending on the specific surface area of electrodes.

According to the E–pH diagram of cobalt [69] and research results in [68], the associated chemical reactions on the cobalt electrode surface in relation to phosphate measurements can be explained. Before the cobalt electrode test for phosphate detection, the electrode was immersed in DI water for approximately 24 h as pretreatment to form a layer of CoO on the electrode surface. The process is described as Reactions (13) and (14): the water molecules are adsorbed on the electrode surface first, and then cobalt atoms are oxidized to form Co(OH)$^+$ ions. Under neutral condition (pH 7.0), the Co(OH)$^+$ ions then react with water molecules further to form a passive CoO film on the electrode surface (Reactions (16) and (17)).

After the pretreatment, the cobalt electrode is tested in an acidic buffer (25 mM KHP, pH 4.0). Under acidic condition, the passive CoO film is reactivated to release Co$^{2+}$ ions:

\[ \text{CoO} + \text{H}^+ \rightarrow \text{Co(OH)}^+ \] \hspace{1cm} (33)
\[ \text{Co(OH)}^+ + \text{H}^+ \rightarrow \text{Co}^{2+} + \text{H}_2\text{O} \] \hspace{1cm} (34)

When the phosphate ions ($\text{H}_2\text{PO}_4^-$) are present in a solution, they combine with Co$^{2+}$ ions to form a layer of Co$_3$(PO$_4$)$_2$ on the electrode surface (Reactions (21)–(23)).

Therefore, phosphate detection using cobalt is possible from the cobalt electrode oxidation processes (Equations (2), (5), (6) and (7)) in an acidic condition by combining Co$^{2+}$ ions with phosphate ions in the solution into Co$_3$(PO$_4$)$_2$ on electrode surface. The passive CoO film plays an important role in the phosphate sensing process as a medium film between cobalt and solution. It is hypothesized that the CoO film serves as a “solid electrolyte” consisting of Co$^{2+}$ and O$^{2-}$ ions that maintains a steady concentration zone of Co$^{2+}$ and O$^{2-}$. Ions ($\text{H}^+$ and $\text{H}_2\text{PO}_4^-$) in the solution will diffuse into CoO film, affecting the concentration of Co$^{2+}$. Without CoO film on the surface, the Co$^{2+}$ ion concentration will be easily affected by solution conditions in which a stable current signal is not achieved.
To discuss the electrochemistry process on the electrode, Equations (13), (14), and (15) can be simplified and presented as

\[ \text{Co}^{2+} + 2e^- \overset{k}{\rightarrow} \text{Co} \]  

(35)

following the format of \( O^z + ne^- \overset{k}{\rightarrow} R_{z'} \) [72]. The oxidation current signal in the CV test is the total current arising from the electrochemical process of Co (Equation (35)), which can be described by the Butler–Volmer equation [72] and capacitance charging process at the electrode surface:

\[ i = i_{\text{oxidation}} - i_{\text{capacitance charging}} \]  

(36)

\[ i_{\text{oxidation}} = FAK_0^0 \left[ C_0(0, t) \exp(-\alpha f(E - E_0)) - C_R(0, t) \exp((1 - \alpha) f(E - E_0)) \right] \]  

(37)

where \( F, A, k^0 \) and \( \alpha \) represent the Faraday constant, area of the electrode, rate constant and transfer coefficient, respectively. \( f = R/T \), where \( R \) and \( T \) are the gas constant and temperature, respectively. The first term in Equation (37) is the anodic current, and the second term stands for the cathodic current. \( C_0(0, t) \) is the concentration of \( \text{Co}^{2+} \) on an electrode surface at time \( t \), and \( C_R(0, t) = C_{\text{Co}} = 1 \) because Co in solid state is standard state \((\text{Co}_\text{st})\). \( E \) is the potential applied between the working electrode and the reference electrode. \( E_0 \) represents the open-circuit potential between them in equilibrium.

Because \( C_R(0, t) = C_{\text{Co}} = 1 \), the cathodic current (second item in Equation (37)) is independent of any ion concentration in solution. On the other hand, the cathode current arising from the reduction of \( \text{Co}^{2+} \) is negligible in the oxidation current. Therefore, only anodic current can be discussed:

\[ i_{\text{anodic}} = FAK_0^0 \left[ C_0(0, t) \exp(-\alpha f(E - E_0)) \right] \]  

(38)

This shows that the oxidation current in the CV test (Figure 27) is related to the \( \text{Co}^{2+} \) concentration on an electrode surface. In the planar electrode surface, owing to the limited surface area and reaction rate, Reactions (21)–(23) are not dominant, so the \( \text{Co}^{2+} \) ion concentration at the electrode surface does not change.
significantly (no oxidation peak was observed). Therefore, the CV current response for a planar electrode reflects the change in capacitance charging current due to a change in the absorbed phosphate ion concentration at the electrode surface.

For the nanostructured electrode, the rate of Reactions (21)–(23) is enhanced owing to an increased surface area and resultant reaction sites. Therefore, the Co$^{2+}$ ion concentration at the electrode surface is decreased when phosphate ions are present in solution. This leads to an enhanced rate of Equations (13) and (14). This explains the increased oxidation peak currents near -0.4 V vs. Ag/AgCl with the increased phosphate concentrations. In this case, the change in anodic current dominates the change in capacitance charging current so that a decrease of CV oxidation currents was observed, which responds to the increased phosphate concentrations according to Equations (36) and (37).

4.5 Conclusion

Using the hydrothermally grown ZnO nanoflake template and electroplating methods, high-surface-area nanostructured Co electrodes were designed and fabricated for phosphate sensing. Thin cobalt alloy films were electroplated from an electroplating bath that contains CoSO$_4$ only on a silicon substrate. Through electroplating, ZnO nanoflakes were covered by a cobalt layer and were selectively etched to finalize nanostructured cobalt electrodes. The surface compositions and morphologies were characterized using EDS and SEM, respectively. The fabricated sensors were tested in standard KH$_2$PO$_4$ solutions with various phosphate concentrations. The finished nanostructured cobalt electrode showed improved LOD (1×10$^{-6}$ to 1×10$^{-3}$ M) compared to the planar cobalt electrode. It is expected that the increased surface area and relatively simple fabrication protocols would make the proposed method attractive and promising for many environmental sensing applications. The different sensor responses observed from planar and nanostructured sensors were explained in relation to the intermediate reaction mechanisms on electrode surfaces.
5.1 Introduction

During recent decades, there has been an increasing demand and emerging market for highly sensitive gas detection devices with various applications such as toxic/flammable gas sensors, smoke detectors and indoor air quality monitors [75]. Considerable research effort aiming at the development of cost-effective microsensor technologies has been undertaken to replace conventional expensive, labor-intensive and time-consuming analytical methods such as optical spectroscopy and gas chromatography.

Among these efforts, conductometric sensors based on metal oxides have been successfully implemented into commercial products owing to their high sensitivity, low cost and applicability to compact device integration [76]. Current commercial sensors typically utilize oxide thick films with polycrystalline structures, which usually work at an elevated temperature to enhance chemical reactions at the metal oxide surface. This increases the power consumption and complexity because additional heating elements are required.

In contrast to conventional polycrystalline metal oxide gas sensors, nanomaterial-based devices with small feature dimensions, high area-to-volume ratio and high crystallinity have demonstrated great potential for next-generation sensor development. Several enhanced sensor characteristics such as high sensitivity, highly directional electron transfer ability, and low detection limit could be found [77]. Various synthesis routes, such as chemical vapor deposition [78], chemical conversion [79], sol-gel deposition [80], electrodeposition [81], reactive sputtering [82], spray-pyrolysis [83], and thermal oxidation [84], were proposed to produce various nanostructures for further improving their sensing characteristics. CuO nanowires synthesized by thermal oxidation have shown good potential for chemical sensors owing to their high surface area/volume ratio, long-term stability associated with high crystallinity [85] and possibility for
on-chip synthesis [86], which are advantageous for developing integrated microsensors with high sensitivity and rapid response [87].

Metal oxide nanowire gas sensors can even obtain multi-analyte gas sensing abilities by modification of catalytic agents, which are specific to a certain gas species. For example, catalytic metal nanoparticles (typically Pd, Pt or Au) were applied for surface modification of multiple- [86] and single-nanowire [88] devices, which showed improved gas sensing performance even at room temperature [89]. There have already been some promising results showing the ability to realize a miniaturized gas sensor system through a combination of the catalytic modification approach and the use of various oxide materials. For example, discrimination of hydrogen and carbon monoxide has been achieved by individual nanowires of different metal oxide materials [90]. A similar result was reported in which the distinction among nitrogen dioxide, ethanol and hydrogen was achieved by a sensor array consisting of metal oxide nanowires and single-walled carbon nanotubes [91]. Arising from two different transduction mechanisms (nanowire channel resistance and nanowire–nanowire junction barrier), the signal statistical variation plays a major role in the sensor device’s discrimination power [92]. These nanowire-based gas sensors show great potential in abilities for considerable device miniaturization and also provide novel sensing concepts based on the one-dimensional nanostructures.

Although single-nanowire-based devices have shown better sensing performance, building reliable electrical contacts on a single nanowire calls for complex fabrication and difficult manipulation processes with a low yield, which has imposed a great limitation on the practical implementations. For example [24], InAs nanowires were synthesized first, and a single wire was transferred to the silicon wafer surface. A series of Au/Ti contact patterns with a 30-nm gap were deposited by sputtering on the nanowire. This integration process requires high-resolution alignment and accurately controlled deposition, which are expensive and labor intensive. Moreover, owing to the fluctuation of properties from one to another single
nanowire, the device is susceptible to poor reproducibility. Therefore, multiple-nanowire sensors based on an interdigitated configuration are more promising for realistic applications.

On the other hand, nanowire-based sensor performance is mainly related to the interfacial behavior at the junction of sensing materials and electrodes. Usually, in order to enhance the nanowires’ contribution in the detected signal, Schottky contacts are avoided through certain modulation technique. However, recent research has indicated that Schottky contacts showed better performance as highly sensitive sensors for certain applications [93, 94]. Therefore, modulating the electrical junction properties of the nanowire-based sensors provides extra means to enhance the sensor performance in addition to improving the sensing materials themselves. This is usually achieved by introducing electrode materials with varying work functions [95] or adjusting the work function of nanowires with other materials [88], which usually increases the complexity of the fabrication process. In this work, we propose a facile process based on electrode geometry and electroplating time (thus, electrode thickness) adjustment that can modulate the junction properties of on-chip CuO nanowires produced by electroplating and thermal oxidation.

In this work, a batch fabrication process for CuO nanowire-bridged interdigitated electrodes for toxic/flammable gas sensing is developed. The device integration process was achieved by a combination of photolithography, electroplating and thermal oxidation techniques.

5.2 Fabrication

5.2.1 Copper Electroplating and Thermal Oxidation

With the standard photolithography process [96], a 40-µm-thick AZ40-XT photoresist (PR) with a 4 × 9 array of 3 mm diameter circular openings was coated on a 3-inch Au/SiO₂/Si wafer. With optimized Cu electroplating parameters for microfabrication [97], the patterned wafer as a cathode was connected with a Cu foil anode, and both electrodes were soaked in 0.5 M CuSO₄ electrolyte under stirring condition. From row 1 to 9 in the array, a 30 mA/cm² current was applied for 1 to 9 min, in sequence. The wafer was then washed by acetone and DI water to strip the PR and dried by nitrogen.
With the electroplated Cu patterns, the stylus profiler (DektakXT) was used to measure the Cu film thickness and surface roughness (stylus type/force: 2 μm/3 mg, scan length/resolution: 200 μm/0.033 μm/point). The wafer was then placed on a hotplate heated to 500 °C for 200 min and cooled in atmosphere. The oxidized film was characterized by thin film x-ray diffraction (TF-XRD, Empyrean Series 2).

5.2.2 Device Fabrication

As the schematics show, with the standard photolithography process [71], Au-interdigitated electrodes with 20 μm digits/8 μm gap and different digit numbers (5, 10, 20, 40, 80 and 160 digits) were fabricated (Figure 29 (a)-(d)). To confine the Cu growth on Au digits, the same photolithography process was carried out on the fabricated Au electrodes (Figure 29 (e), (f)). The patterned wafer as a cathode was connected with a Cu foil anode, and both electrodes were soaked in 0.5 M CuSO₄ electrolytes under a stirring condition. The Cu...
pattern was electroplated on top of Au digits with 30 mA/cm$^2$ current for 1, 2 and 3 min (Figure 29 (g)). After stripping the PR with acetone, the electrodes were thermally oxidized under 500 °C for 200 min and cooled in atmosphere (Figure 29 (h), (i)). The Cu pattern before and after oxidation was characterized by thin film x-ray diffraction (TF-XRD, Empyrean Series 2, PANalytical B. V.). The electrode morphologies were then obtained by scanning SEM (ZEISS Ultra-55), and the I–V responses were characterized by a Keithley 2401 sourcemeter (Tektronix).

5.3 Gas Sensing Performance Characterization

![Test Chamber](image)

Figure 30 Gas sensing performance characterization setup.

As shown in Figure 30, with the fabricated electrode, the gas sensing performance at room temperature was carried out in an enclosed chamber. Cu wires were bonded to the electrode contact pads and connected to the sourcemeter (Keithley 2401) measuring the resistance. The sensor’s response was characterized by pumping in the saturated ethanol vapor into the chamber followed by pumping in air for recoverability characterization.
5.4 Results and Discussions

5.4.1 Copper Electroplating
The thickness and surface roughness measurement results of the electroplated Cu array are shown in Figure 31 (a). Faraday’s Law [98] was applied to give out an expected thickness of Cu film electroplated with 30 mA/cm$^2$ current for different times. It was observed that after 3 min, the Cu film showed a much slower growth rate compared with the thickness predicted by Faraday’s Law. This is because Faraday’s Law gives only a prediction of the amount of electroplated Cu, and the thickness was calculated by dividing the amount of Cu by its density, under the hypothesis that the electroplated film has a perfectly flat and smooth surface. However, as shown in Figure 31 (a), the surface roughness also increased with electroplating time, which indicates an increased actual surface area. Therefore, after 3 min, the actual current density was much smaller than 30 mA/cm$^2$, which explains the low growth rate of Cu film. Hence, long-time electroplating is not energy efficient and wastes power on increasing surface roughness, which is also bad for micro devices owing to low uniformity. Based on this, we performed electroplating within 3 min for device fabrication.

The results of TF-XRD for film content characterization are shown in Figure 31 (b) and (c). It can be seen that the peak intensity of Au did not change after thermal oxidation, which indicates stable electric conductivity of the Au circuit. The Cu peak vanished after thermal oxidation while a clear pattern of CuO was observed, without any possible pattern of Cu$_2$O presented in [99]. This is because the sample thickness is thin (less than 2 μm), so the Cu film is thoroughly oxidized, as described in Reactions (39) and (40).
Figure 31 Copper electroplating and thermal oxidation results: (a) thickness and surface roughness characterization and TF-XRD pattern (b) before and (c) after thermal oxidation.

5.4.2 Device Fabrication
The electroplated Cu pattern (10-digit electrode) was characterized by a KEYENCE 3-dimensional microscope profiler, and the results are shown in Figure 32. With 1 min of electroplating, a layer of 0.93
μm thick Cu was electroplated uniformly on Au digits, and the gap distance between digits was approximately 8 μm. With 2 min and 3 min electroplating time, the Cu pattern thickness was effectively increased to 2.50 μm and 3.94 μm, respectively, whereas the gap distance was slightly decreased by less than 1.5 μm without greatly changing the electrode configuration.

Figure 32 Geometry parameters of Cu pattern electroplated for (a) 1 min, (b) 2 min and (c) 3 min. However, the thickness of the Cu pattern with different digit numbers showed a decreasing trend with increasing digit number, as shown in Figure 33. This clearly indicates that longer electroplating time results
in an overall thicker pattern, whereas for each electroplating time, a small digit number electrode obtained a more effective deposition of Cu than a larger digit number electrode.

![Figure 33 Cu pattern thicknesses with different digit number electrodes.](image)

To understand this phenomenon, a simulation (COMSOL Multiphysics) based on a simplified model was carried out, and the result is presented in Figure 34. In this model, only 1-, 3- and 5-digit situations (gray squares are locations of digits for electroplating) with the same parameters (concentration and electroplating current density) were used to study the process. The color legend indicates the concentration distribution of Cu$^{2+}$ ions in the electrolyte during electroplating, and the redline plot indicates the Cu$^{2+}$ ion concentration.
at the electrode surface. Both the color legend and redline plot indicate an obvious Cu$^{2+}$ ion depletion region at the digit surface. This reveals that compared with the 1-digit situation, the 5-digit electrode occupying more space consumed the Cu$^{2+}$ faster, leading to a wider depletion region. Therefore, a large digit number electrode suffered more severe Cu$^{2+}$ ion depletion, which greatly limited the Cu source supply for electroplating and therefore cause a slower deposition rate.

Figure 34 Simulation of Cu pattern electroplating with 1-, 3- and 5-digit situations.

After the Cu pattern electroplating, the wafer was placed on a hotplate for thermal oxidation, and the fabricated electrodes are shown in Figure 35. The morphologies of the electrode microstructures were characterized by SEM. Ten-digit electrodes with different electroplating time were selected to illuminate the changes of microstructures and morphologies as shown in Figure 36. A clear trend of increasing CuO nanowire density and decreasing digit gap distance with electroplating time is shown. According to these results and a CuO nanowire growth mechanism [99, 100], during the thermal oxidation process, a Cu$_2$O layer is formed first and then a CuO layer is grown on top, as shown in Reactions (39) and (40). The mass
transport routes and nanowire growth mechanism during the oxidation process are briefly shown in Figure 37 [100]: during the oxidation process, the Cu\(^+\) ions diffuse through the CuO grain boundaries to the outer surface and then diffuse to the tip of the initiated nanowires along the surface driven by the surface concentration gradient, leading to growth of the nanowire in both length and diameter. The oxidation product and morphologies are significantly affected by the oxidation temperature. For oxidation at low temperatures (<250 °C), the mobility of Cu cations and vacancies is too low to active a fast reaction at the CuO/Cu\(_2\)O interface to generate enough interfacial stress to drive the grain boundary diffusion for the growth of nanowires; on the other side, with high-temperature oxidation (> 700 °C), the lattice diffusion dominates the grain boundary diffusion, which releases the interface stress quickly, generating a uniform growth of CuO grains rather than nanowires. Therefore, an intermediate temperature, 500 °C, was chosen for the oxidation temperature in this work.

![Figure 35 The fabricated microsensor electrode (10-digit and 80-digit electrodes).](image-url)
Figure 36 SEM results of 10-digit electrode with (a) 1 min, (b) 2 min and (c) 3 min of electroplating.

\[ 4Cu + O_2 \overset{500^\circ C}{\longrightarrow} 2Cu_2O \]  \hfill (39)

\[ 2Cu_2O + O_2 \overset{500^\circ C}{\longrightarrow} 4CuO \]  \hfill (40)
Figure 37 Mass transport mechanism of Cu\(^{2+}\) ions for CuO nanowire growth. [100].

In addition to the temperature’s effect on morphologies, from the diffusion mechanism shown in Figure 37, it is expected that the thickness of the Cu pattern also plays an important role. In contrast to [99] where thick Cu foil (0.5 mm) was used, in this work, the electroplated Cu pattern is thin (less than 4 \(\mu\)m). Therefore, the limited supply of Cu cations from this thin film could significantly impact the formation of the CuO layer and nanowires (density and length) during the oxidation process. In addition to this enhancement effect, owing to the expansion of the Cu pattern after being oxidized to CuO, thicker Cu patterns provide a sufficient Cu source to form a thicker CuO layer such that the gap between digits was further narrowed so even short nanowires could bridge electrodes to form a conduction path.
5.4.3 Electrical Property Characterization

**Figure 38 Interdigitated electrodes electrical properties characterization results: I–V characterization of electrode with Cu electroplated for (a) 1 min, (b) 2 min, (c) 3 min and (d) electrode resistances.**

I–V characteristics were obtained by a sourcemeter in the range of -5 to 5 V, as shown in Figure 38. Owing to the low nanowire bridge density in the first group of electrodes (1 min electroplating), only electrodes with 5, 10 and 20 digits showed responses, whereas others exceeded the measurement range of the sourcemeter (Figure 38. (a)). The I–V response of the second (2 min electroplating) and third (3 min electroplating) group electrodes were presented, in which a transition of ohmic to Schottky contact was observed, respectively (detailed I–V curves after transition are shown in insets). The resistances of all electrodes are shown in Figure 38 (d). For the second and third groups of electrodes, with increased digits, the resistance decreased in the ohmic contact range and started to increase after the transition occurred. As
the schematic shows in Figure 39, the conducting behavior of the electrodes is controlled by two factors: CuO/Cu-Au interfaces contribute to Schottky behavior, and effective CuO nanowire bridges contribute to ohmic behavior.

Figure 39 Schematics of charge conduction path between the interdigitated Au electrode through Schottky barrier and CuO nanowire bridges.

In this simplified model, with the small digit numbers, nanowire bridges played a dominate role in the device electrical behavior. Under this situation, the device has ohmic contact, and the resistance decreases
with increasing digit number. When the digit number is increased, the CuO/Cu-Au interface area is enhanced to become the dominant factor. Under this situation, the device features Schottky contact, and the resistance increases with increasing digit number. Finally, comparing the three groups of devices, the CuO nanowire bridge density increased with increasing Cu pattern thickness as observed in Figure 36, which led to an overall decrease of device resistance.

5.4.4 Gas Sensing Performance
The sensor’s response to saturated ethanol vapor and recoverability characterization at room temperature are shown in Figure 40. The electrode’s relative resistance defined in Equation (41) was applied for gas sensing behavior characterization.

\[ S = \frac{R_{\text{ethanol}} - R_{\text{air}}}{R_{\text{air}}} \times 100\% \]  

(41)

![Figure 40 Sensor response to saturated ethanol vapor and recoverability characterization at room temperature.](image)
The result shows that after the ethanol saturated vapor was pumped into the chamber, the sensor’s relative resistance started to increase and stabilized after 2500 s. The air was then pumped into the chamber for recovery. It was observed that the relative resistance returned to the original value with approximately 500 s of recovery time. The same process was repeated for the cycle test, indicating the sensor’s multi-application ability. The sensing mechanism is briefly shown in Figure 41.

![Figure 41: The mechanism of CuO nanowire sensing behavior to saturated ethanol vapor.](image)

According to the proposed mechanism in [101, 102], the oxygen molecules (O₂) are first adsorbed on the surface of the CuO nanowire, forming a conduction layer consisting of high-concentration holes (h⁺), which are the major charge carriers. When the reductive gas molecules are present, they adsorb on the nanowire surface and react with the adsorbed O₂⁻ ions, consuming the holes and resulting in a reduced depth of the conduction layer, which is indicated by the increased sensor resistance.

5.5 Conclusion
CuO-nanowire-based devices fabricated with varying Cu electroplating time and electrode configuration exhibited I–V characteristics that represent Schottky or ohmic junction behavior depending on their processing conditions. Without introducing additional materials or processing steps, the device resistance control could be achieved by tuning the CuO nanowire bridge density related to Cu pattern thickness, and the contact behavior transition could be achieved by tuning the CuO/Cu-Au interface area related to the electrode digit number. A simple model was also proposed to describe the transition of I–V characteristics for better understanding the dominant mechanism in relation to the process conditions. The fabricated
sensor electrode showed reliable sensing performance to saturated ethanol vapor with good recoverability at room temperature. For future work, an asymmetric configuration can be studied for further modulation without using extra dopants or electrode materials in the device and the sensing ability of other gas species.
CHAPTER SIX: FUTURE WORK

6.1 A Rapid in-situ Electrochemical Surface Modification Process for Nanostructured Gold Electrodes

In the previous work, planar Au electrode was applied as a cathode on where nanostructured metals and metal oxides were deposited. Besides the metals such as Co and Cu used in this dissertation, Au itself is also widely applied in the areas of biosensors [103], bioelectrochemical sensing [104, 105], and analytical chemistry [106]. A variety of strategies, such as alloying and dealloying [107], chemical reaction and assembly [108], and electrodeposition [109], were used for nanostructured Au electrode fabrication. However, these methods are limited due to expensive processes and complex additives. Therefore, we are proposing to develop a simple and fast in-situ electrochemical surface modification process of the planar gold electrode. This in-situ electrochemical modification process is inspired by the electrochemical migration phenomenon [110]. It is hypothesized that this high efficiency formation mechanism is based on electrochemical dissolution of cations from and redeposition to the electrode surface.

Based on the preliminary experiment results, high density nanodendrites were obtained on the planar gold electrode surface showing enhanced surface area and electrochemical activity. In the future work, the applicability of the modified electrode in sensor application will be explored. And, the nanodendrites structure can be applied as template for secondary nanostructured metal deposition.
6.2 Synthesis of $p$-$CuO$ nanowire/$n$-$ZnO$ nanosheet Heterojunctions by Electroplating and Thermal Oxidation Process

Besides the results presented in Chapter 5 based on $CuO$-$CuO$ nanowire bridge configuration for gas sensor, building up the heterostructures between two different metal oxide semiconductors was also demonstrated as an efficient strategy to improve the gas sensing performance due to the charge separation effect. Among these efforts, $CuO$/ZnO heterojunctions attract great research interests because of their unique electrical properties. However, the currently developed devices are limited by the configuration and material morphologies. Therefore, based on the developed method in Chapter 5, we are proposing to develop a simple fabrication route for $p$-$CuO$/$n$-$ZnO$ heterojunction based device with well-defined configuration though a similar photolithography, electroplating and thermal oxidation processes as preliminary attempt for high quality gas sensor development.

According to the preliminary results, it revealed that $CuO$ nanowires and ZnO nanosheets could be achieved through the thermal oxidation process of the electroplated Cu and Zn. With the same interdigitated electrode configuration, Cu and Zn patterns were electroplated first and through the thermal oxidation, $p$-$CuO$ nanowire/$n$-$ZnO$ nanosheet heterojunction were obtained which was confirmed by SEM and I-V characterizations. Based on these results, the electrode morphologies, junction properties and gas sensing performance will be further explored and optimized in the future work.
APPENDIX A: SILICON WAFER PREPARATION PROCESS
This appendix contains the detailed steps for the silicon wafer preparation process.

1. Substrate: 3-inch <1 0 0> single-side polished N-type silicon wafers

   ![Silicon Wafers]

2. Wet oxidation process

   ![Oxidation Equipment]

   Furnace temperature: 1000 °C (90 min oxidation, SiO$_2$ thickness: 5000 Å)

   N$_2$ pressure: 5 psi

   Flow rate: 1.0 on flowmeter scale

   Bubbler temperature: 95–99 °C

   Push-in/pull-out rate: 3 min
3. Electron beam (E-beam) deposition of Ti seed layer and Au layer

Ti seed layer thickness: 100 Å

Au conduction layer thickness: 1000 Å

Note: The push-in/pull-out rate should be precisely controlled in the wet oxidation process. An overly high rate may lead to cracking of silicon wafers. The E-beam deposition of the Ti seed layer and Au layer should be deposited in sequence without interruption. Exposing the Ti seed layer deposited wafer in air leads to oxidation of Ti and then poor adhesion and quality of the Au layer on top.
APPENDIX B: PHOTOLITHOGRAPHY PROCESS OF PHOSPHATE SENSOR ELECTRODE
This appendix contains the detailed photolithography process steps for the phosphate sensor electrode fabrication.

Substrate: Au/Ti layer deposited silicon wafer prepared by following appendix A.

1. Clean base.
2. Spin coat Shipley 1813 photoresist (10 s. at 500 RPM, 47 s at 3000 RPM) for 1.3-μm-thick patterns.
3. Let sit at room temperature for 3 min.
4. Soft bake: hotplate at 105 °C for 3 min.
5. Let sit at room temperature for 3 min.
6. Align and expose.

EVG 620 Aligner

Load the mask by a mask holder → load the PR-coated wafer by wafer chuck → UV exposure for 8 s at 12 mW/cm² → unload the exposed wafer → unload mask

7. Develop for 40 s in a developer (MIF CD-26).
8. Microscopy observation.

9. Hard baking at 105 °C for 10 min.

10. Place the wafer in Au and Ti etchant in sequence for electrode patterning and clean with DI water.

11. Clean with DI water.

12. Remove photoresist using acetone-methanol-DI water.
APPENDIX C: PHOTOLITHOGRAPHY PROCESS OF CUO NANOWIRE-BASED SENSOR ELECTRODE
This appendix contains the detailed photolithography process steps for the CuO nanowire-based sensor electrode fabrication.

Substrate: Au/Ti layer-deposited silicon wafer prepared by following Appendix A and photolithography process carried out following Appendix B.

1. Clean base.
2. Spin coat Shipley 1813 photoresist (10 s at 500 RPM, 47 s at 3000 RPM) for 1.3-μm-thick patterns.
3. Let sit at room temperature for 3 min.
4. Soft bake: hotplate at 105 °C for 3 min.
5. Let sit at room temperature for 3 min.
6. Align and expose.
   
   EVG 620 Aligner
   
   Load the mask by mask holder → load the PR coated wafer by wafer chuck → UV exposure for 8 s at 12 mW/cm² → unload the exposed wafer → unload mask
7. Develop for 40 s in a developer (MIF CD-26).
8. Microscopy observation.
9. Hard baking at 105 °C for 10 min.
10. Place the wafer in Au and Ti etchant in sequence for electrode patterning and clean with DI water.
11. Clean with DI water.
12. Remove photoresist using acetone-methanol-DI water.
13. Second layer.
14. Spin coat Shipley 1813 photoresist (10 s at 500 RPM, 47 s at 3000 RPM) for 1.3-μm-thick patterns.
15. Let sit at room temperature for 3 min.
16. Soft bake: hotplate at 105 °C for 3 min.

17. Let sit at room temperature for 3 min.

18. Align and expose. Align the second layer mask to the patterned Au electrode.
   
   EVG 620 Aligner
   
   Load the mask by mask holder → load the PR-coated wafer by wafer chuck → UV exposure for 8 s at 12 mW/cm² → unload the exposed wafer → unload mask

19. Develop for 40 s in a developer (MIF CD-26).

20. Microscopy observation.

21. Hard baking at 105 °C for 10 min.

22. Connect wafer as cathode with Cu foil anode and keep both electrodes in 0.5 M CuSO₄ electrolyte.
   
   Electroplate Cu pattern on patterned Au electrode. Current density is 30 mA/cm².

23. Clean with DI water.

24. Remove photoresist using acetone-methanol-DI water.

25. Place the wafer on hotplate at 500 °C for 200 min and then cool in air.
REFERENCES


