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Fabrication of Ultra-Fine Cathodes For Cold-Field Emission

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ABSTRACT

FABRICATION OF ULTRA-FINE CATHODES FOR COLD-FIELD EMISSION

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This thesis discusses the different fabrication steps involved in producing ultra-fine cathodes that are suitable for cold-field emission. A four-step nanofabrication process has been developed to obtain the cathodes with tip diameters ranging from 10nm to 20 nm. First, a mask is patterned on a 2-inch silicon wafer using monodisperse 1.18µm silica spheres. These particles are self-assembled using vortex-flow-enabled assembly technique to form close-packed monolayers. Then the silicon is etched using reactive ion etching technique. An inductively coupled plasma etcher is used to perform anisotropic and isotropic etching. The etching recipes used are chosen such that they are more selective to silicon compared to silica to form smooth hour-glass-shaped pillars. These pillars are further sharpened by eliminating the silica mask using a buffer oxide etch solution and then sharpening the necks of the pillars through multiple oxidation steps. Various oxidation times are tested to achieve fine aspect-ratio cathodes. To improve the field enhancement factor and to increase the wear resistance of the silicon cathodes, a 25nm tungsten film is deposited on which a diamond film is deposited through chemical vapor deposition. The fabricated cathodes are tested under ultra-high vacuum conditions for field emission under an applied electric field of 3KV-6KV. Thereby, the field enhancement factor for these cathodes is calculated using Fowler-Nordheim equations.
FABRICATION OF ULTRA-FINE CATHODES FOR COLD-FIELD EMISSION

BY

SRUJANA VALLURI

A THESIS SUBMITTED TO THE GRADUATE SCHOOL
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DEDICATION

To my beloved husband and son, parents, near and dear
TABLE OF CONTENTS

LIST OF TABLES .........................................................................................................................vii
LIST OF FIGURES .....................................................................................................................viii

1. INTRODUCTION ....................................................................................................................... 1
   1.1 Cold-Field Emitters ........................................................................................................... 1
   1.2 Literature Survey ............................................................................................................. 2
   1.3 Thesis Overview ............................................................................................................... 5

2. THEORY ................................................................................................................................. 6
   2.1 Cold-Field Emission ....................................................................................................... 6
   2.2 Applications ................................................................................................................... 8
   2.3 Objectives ...................................................................................................................... 8

3. NANOSPHERE LITHOGRAPHY .............................................................................................. 9
   3.1 Self-Assembly at Air-Water Interface ............................................................................. 9
      3.1.1 Langmuir Blodgett (LB) Films .............................................................................. 10
   3.2 Silica Deposition Technique ......................................................................................... 10
   3.3 Fabrication .................................................................................................................... 12
      3.3.1 Surface Functionalization of Silica ....................................................................... 13
      3.3.2 Particles with High Monodispersity .................................................................. 14
      3.3.3 Silica with Methacrylate Termination ............................................................... 14
      3.3.4 Surface Functionalization Using Mercaptopropyl .. ........................................... 15
      3.3.5 Particle Filtration ............................................................................................... 17

4. REACTIVE ION ETCHING ....................................................................................................... 20
   4.1 Etching ........................................................................................................................... 20
   4.2 ICP-RIE ......................................................................................................................... 22
   4.3 Fabrication Using RIE ................................................................................................. 24
   4.4 Anisotropic Etch .......................................................................................................... 24
   4.5 Deep Cl$_2$ Etch ........................................................................................................... 26
      4.5.1 Data Analysis, Results and Observations ......................................................... 27
   4.6 Deep Cl$_2$ Etch Using a Patterned Cr Mask .............................................................. 31
   4.7 Isotropic Etch .............................................................................................................. 32
      4.7.1 Effect of Process Parameters on the Etch Rate .................................................. 36
LIST OF TABLES

Table 1: Parameters for Chloride Punch Recipe for Anisotropic Etch ........................................... 24
Table 2: The Etch Profile of the Chlorine Punch Recipe for Different Time Durations ................. 25
Table 3: Etch Profile Results Using Deep Cl₂ Etch ........................................................................ 29
Table 4: Parameters of the Silicon Isotropic Etch Recipe .............................................................. 33
Table 5: Tabulated Results for the Neck Diameters Obtained for Various Etch Times ............. 34
Table 6: Neck Diameters at Various Individual Gas Compositions and Etch Duration .......... 38
Table 7: The Oxide Growth and the Amount of Silicon Consumed for Different Durations of Oxidation on Plain Silicon Wafer .............................................................. 47

Table 8: Table to Calculate the Normal Distribution of the Tip Diameters ............................... 52
Table 9: Composition of Gases Used for N-UNCD Deposition ..................................................... 54
Table 10: Comparative Study .................................................................................................... 65
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Energy-band diagram of different types of emissions.</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Schematic illustration of the vortex flow-based assembly of ordered close-packed monolayers of nanospheres.</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>Assemblies formed using Cospheric 1.18µm monodisperse silica spheres mixed with 700µL of ethanol and 500µL of DI water. Some areas with agglomerates are seen in the picture at 10x magnification.</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>Assemblies formed from Sol1 that has been sonicated for 30 min with the MPTMS. Taken at 50x magnification.</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>Assemblies from the Sol2 which is sonicated 30 +30 min with MPTMS. Both images are at 50x magnification.</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>Top view of the assemblies when seen under a microscope. The image is taken at 250x magnification.</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>Process showing ion bombarding the wafer during dry physical etch.</td>
<td>21</td>
</tr>
<tr>
<td>8</td>
<td>Process showing ion interaction with the substrate material in dry chemical etching.</td>
<td>22</td>
</tr>
<tr>
<td>9</td>
<td>Graph showing the anisotropic etch profile of the silicon pillars using the punch recipe.</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>Cross-sectional SEM image of the silicon wafer after 5 min of etch shows that the silica spheres have minimal etch while a significant etch can be observed on the silicon substrate.</td>
<td>26</td>
</tr>
<tr>
<td>11</td>
<td>Cross-sectional SEM of the sample after the deep Cl₂ etch. Image (a) shows structures after 6min, (b) shows 6+3min, (c) is 6+3+3min and (d) shows 6+3+3+3 min.</td>
<td>28</td>
</tr>
<tr>
<td>12</td>
<td>Graph showing the etch rate of silicon.</td>
<td>30</td>
</tr>
<tr>
<td>13</td>
<td>Graph showing the etch rate of silica.</td>
<td>30</td>
</tr>
<tr>
<td>14</td>
<td>Illustrating the accompanying lateral etch when using chloride etch.</td>
<td>31</td>
</tr>
</tbody>
</table>
Figure 15: Patterned Si wafer using photolithography. ................................................................. 31

Figure 16: SEM images of the Cr-deposited sample after 15 min of anisotropic Cl₂ etch .......... 32

Figure 17: Cross-sectional SEM images of the hour-glass-shaped structures formed after 2 min 45sec of Si isotropic etch. ............................................................................................................. 34

Figure 18: Graph showing the etch profile using SF6 and Ar gases. .......................................... 35

Figure 19: SEM image of sample that has been over-etched as the silica mask is lifted off after 2min of etch. ........................................................................................................................................ 36

Figure 20: SEM image showing the cross-section of the sample after 6 min of Anisotropic etch and 5min of Cl₂ etch. ........................................................................................................................................ 39

Figure 21: SEM image of sample with AISO 6min, ISO of 20/20 sccm for 5 min, refined ISO of 35/5 for 2min and 40/0 of 2min. ........................................................................................................... 40

Figure 22: SEM image of sample with AISO 6min, ISO of 20/20 sccm for 5 min, refined ISO of 35/5 for 2min and 40/0 of 2+2min. ........................................................................................................... 41

Figure 23: Cross-sectional SEM image of the sample after cleaning with the buffer oxide etch solution showing that all the silica particles have been removed and are oxidation-furnace ready. ........................................................................................................................................ 44

Figure 24: Cross-sectional SEM images of the necks after 5.5hrs of oxidation at 20kx and 40kx magnification respectively. It can be observed that the necks are not completely sharpened. Image (c) is the top-view of the tips after oxidation. ........................................................................................................... 45

Figure 25: Cross-sectional (a,b,c: showing different magnifications) and top-view (d) images of the ultra-fine silicon tips obtained after a total 7.5hrs of oxidation and then etching using HF solution........................................................................................................................................ 46

Figure 26: Image of the sample (say sample A) before and after oxidation and HF etch. The parameters used to form the structures are AISO of 6 min, ISO of 20/20sccm for 5min, refined ISO of 35/5sccm for 2 min and 40/0sccm for 2min........................................................................................................... 48
Figure 27: SEM image of the sample A after further 2hrs of oxidation. ........................................ 49

Figure 28: SEM of sample B, which has been etched using AIS of 6min, ISO of 20/20scm for 5min, refined ISO of 35/5scm for 2min and 40/0 of 2+2min. ................................................................. 50

Figure 29: SEM image of the sample that is patterned using photolithography technique. ........ 51

Figure 30: Plot showing the normal distribution of the cathode tips. ........................................... 52

Figure 31: SEM image of sample (anisotropic etch 6min, isotropic etch 3min 30sec) after 7.5hrs of oxidation at 975°C show a tip curvature of 23nm. ................................................................. 55

Figure 32: SEM image of sample after 25nm of W deposition. ................................................... 56

Figure 33: SEM image of sample after N-UNCD deposition ......................................................... 56

Figure 34: Raman spectra of a plain silicon wafer with N-UNCD film. ........................................ 58

Figure 35: Raman spectra of the sample with N-UNCD film. ....................................................... 58

Figure 36: Schematic view of the DC diode test stand. ................................................................. 60

Figure 37: SEM Image of the sample used for field emission testing. ......................................... 61

Figure 38: I-V characteristics ........................................................................................................ 61

Figure 39: SEM image of the sample after N-UNCD deposition .................................................. 62

Figure 40: Current-voltage characteristics of the UNCD-deposited cathodes ......................... 63
1.1 Cold-Field Emitters:

Controlled electron sources have gained importance recently because of their potential in several technological applications like flat panel displays, micro-electric propulsion systems, information storage devices, and mass spectrometers [1]–[4]. The most common method for producing electron beam from metals is to use high temperatures to emit electrons, called the thermionic effect. Fundamentally, thermionic emission is heating of materials, usually metals, to temperatures typically greater than 1000ºC in order to provide enough energy to the electrons in the conduction band to overcome the emitter’s work function. However, its disadvantages are its high power dissipation, wide energy spectrum of the emitted electrons, and quick degradation of the materials due to the extensively high temperatures. To circumvent the demand for the high thermal energy, cold-field emitters are widely used. Cold-field emission takes place at room temperatures and in the presence of high voltages typically ranging between $10^7$-$10^8$ V/cm. The electrons are emitted from the surface of a metal or a semiconductor through quantum tunneling. The requirement for high electric voltages was quickly overcome by the advancement in research in various semiconducting and nanomaterials like Si, CdTe, CdS, SiC, GaN,, ZnO, carbon nanotubes, graphene, diamond, etc., exhibiting electron emission in the presence of applied electric fields. These materials were found to exhibit field emission properties at low potentials, delivering high current densities usually ranging between 10-100mA/cm² [5].
In this thesis, we explore different fabrication techniques to pattern Silicon to form high-aspect-ratio and high-density arrays of cathodes suitable for field emission and to form structures that withstand high-vacuum environments.

1.2 Literature Survey:

The earliest field-emission cathode was fabricated in 1968 by C.A. Spindt [6] with a low voltage (between 10-100V) and high current of 1.5µA to 6µA. The basic structure consisted of a film of aluminum oxide sandwiched between two molybdenum thin films and mounted on a sapphire substrate. Open micron-sized cavities with a single molybdenum cone are etched on the substrate.

In 1986, G.J. Campisi and H.F. Gray microfabricated a field emission device using orientation-dependent etching [7]. Silicon nitride on a silicon wafer is lithographically patterned on <100> silicon and the underlying silicon is then chemically etched using KOH, H\textsubscript{2}O and isopropanol mixture to form emitters of 1.5µm tall and 10µm spacing between the emitters with tip diameters approximately at 50nm. The emitter rows are patterned with 60µm spacing. The etch profiles are different for different orientations; for example, <100> silicon gave convex pyramidal structures and etching <111> silicon gave concave structures. These tips are coated with SiO\textsubscript{2} and Mo and patterned to form apertures that function as extraction electrodes.

In 1992, C.A. Spindt et al. made a breakthrough using the Spindt cathode arrays for high-frequency operations [8]. Their research on power amplification at high frequencies using field emitter arrays, demonstrated that by fabricating arrays of cathodes with high emitter-tip packing densities in small areas, operation in the gigahertz range can be achieved. Since the cut-off frequency $f_t = \frac{g_m}{2\pi C_g}$, where $g_m$ is the transconductance and $C_g$ is the capacitance of the
device, they patterned the Spindt cathode arrays such that the tips have lower capacitance and high transconductance. The desired capacitance and transconductance is achieved by increasing the emitter packing densities with tip spacing of 4µm and gate apertures of 0.8µm and opting for materials with low dielectric constants, thereby compromising the risk of more frequent cathode failures.

During the same time frame, prospects of different fabrication methods for field emission were explored. In 1992, E.I. Givargizov developed ultra-sharp tips using vapor-liquid-solid (VLS) growth technique [9]. This technique consists of localized deposition of a material substrate using chemical vapor deposition (CVD). In this method, a gold thin film of ~10nm is deposited on a <111> silicon substrate and heated such that a Si-Au liquid solution is formed. Since the liquid film is rather thin, it is broken into small droplets of different diameters. Due to high adsorption of the droplets and the material being abundantly accumulated, they get super-saturated, resulting in the deposition of Si at the liquid-solid interface, which in turn results in the growth of silicon whiskers. These whiskers were later sharpened using oxidation, producing 20-30nm tips. In 1994, J. Liu et al. demonstrated electron emission from diamond-coated Si emitters that were prepared using the VLS technique [10]. Diamond films were deposited using microwave plasma CVD system and proved to exhibit significant field enhancement compared to the pure Si emitters of 30nm tip curvature.

In 2002, gated FEAs of 1nm tip radius and 1µm gate-aperture silicon emitters on <100> silicon were fabricated by Meng Ding and his team [11]. A 250nm layer of SiO₂ on silicon substrate is patterned into 1µm discs and then the underlying silicon is isotropically etched using SF₆ plasma, which is then etched in buffered hydrofluoric acid solution to remove the silica discs. These cones are exposed to multiple cycles of oxidative sharpening to achieve 1nm tip curvatures.
The gate dielectric and the polycrystalline Si gate are later deposited using low-pressure CVD technique.

In the subsequent years, field emitters with different materials like ZnO nanowires, CdS nanowires and diamond-coated emitters were fabricated and studied for their field emission properties [5]. Most of these fabrication methods used Spindt technique and VLS technique [9] and another technique called molding technique, where silicon molds are patterned using anisotropic wet chemical etching and further oxidizing to molds to form cusps onto which metals like molybdenum are deposited and later the molds removed to form sharp tips [12].

Over the years, efforts have been made to develop methods to fabricate gated, dielectric-isolated field emitter arrays to achieve high-aspect-ratio emitters, but by compromising the emitter density. In the recent years with the advancement in microfabrication techniques like nanosphere lithography, plasma-based etching like reactive ion etching (RIE), deep reactive ion etching (DRIE), and plasma enhanced chemical vapor deposition (PECVD) techniques, high-aspect-ratio emitters can be easily fabricated [13]. In 2012, Chi-Chang Wu et al. fabricated silicon nanotip arrays by reactive ion etching <100> silicon coated and patterned with photoresist and subsequent multiple oxidative sharpening steps to obtain tip curvatures of 3nm [14].

During the same time, Ting-Hsuo Chang and his team fabricated nitrogen-doped ultrananocrystalline diamond nanowires for field emission [15]. They deposited polystyrene beads by drop-coating technique on a silicon substrate, Ag thin film is coated, and then the PS beads are removed. The exposed silicon is chemically etched to form silicon nanowires, which are then oxidatively sharpened. The N-UNCD diamond film is then deposited using microwave plasma-enhanced chemical vapor deposition (MPECVD).
1.3 Thesis Overview:

The aim of this work is to fabricate high-aspect-ratio cathodes. So to enable the user to conveniently access the different fabrication steps, this entire thesis is organized accordingly. Chapter 1 deals with introduction to the main topic in discussion, i.e., fabricating cold-field emission cathodes. Various works in this area prior to this research are discussed to give an insight on this work.

Chapter 2 discusses the theoretical concepts of emission and the Fowler-Nordheim equations to study field-emission properties of materials. Chapter 3 gives a detailed description of the nanosphere lithography technique and the vortex-flow self-assembly of silica particles method used in this thesis. Details of etching and reactive ion etching in particular are discussed in Chapter 4. Also, the anisotropic etch and isotropic etch recipes used for fabricating the cathodes are analyzed in detail. Chapter 5 covers the oxidation and wet etching method used to fine tune the silicon pillars obtained through plasma etching. Chapter 6 describes the N-UNCD deposition method and analysis of the diamond films through Raman spectroscopy. Last but not the least, Chapters 7 and 8 are about testing the field-emission properties of the cathodes, their analysis, conclusions and future work.
CHAPTER 2

THEORY

To study the fabrication steps for designing cold-field emitters, the concept and science behind the emitters is to be thoroughly understood. Emission is the excitation of electrons from the surface of a metal when energy equal to the work function of the metal is incident on it. Work function of a metal is the minimum amount of energy required by the electrons to cross the surface potential barrier and escape into vacuum. Types of emissions are classified based on the type of energy delivered to the electrons. If the energy is in the form of heat, it is called thermionic emission. If the incident energy is in the form of photons i.e., light, it is called photoelectric emission and if the emission is due to the energy incident from a secondary source it is called Secondary emission. Field-emission happens when the energy delivered to the electrons is in the form of electric field potential typically in the range of $10^7 – 10^8$ V/cm. This field-emission is prominently used, as emission can happen at room temperature in contrast to the thermionic emission which requires high energies of 1000ºC or greater. Field-emission technology has laid the foundation for vacuum-tubes and revolutionized present-day electronic devices and circuits. In the sections that follow, cold-field emission and its applications are studied in detail to arrive at the specifications of the cathodes that are to be fabricated.

2.1 Cold-Field Emission:

Electron-field emission or cold-field emission (CFE) is the release of electrons in the presence of strong electric fields. When an electric field equal to the work function of the metal is
applied (typically in the range of $10^7 - 10^8$ V/cm), the electrons gain enough energy to cross the potential barrier and tunnel into vacuum. Unlike thermionic emission, cold-field emission happens at room temperature and generates electron densities 1000 times greater. Cold-field emission is a quantum mechanical phenomenon as the electrons tunnel through a deformed potential barrier [16]. The energy-band diagram of electron emission due to different energies as compared to the field-emission is shown in Figure 1 below [17].

![Figure 1: Energy-band diagram of different types of emissions.](image)

CFE is described by a set of mathematical equations called Fowler-Nordheim equations. The FN equations describe electron current density in terms of local work function ($\phi$) and barrier field ($E$). Also, the current density depends on the field enhancement factor which in turn is related to the shape of the emitter [18]. The field enhancement factor ($\beta$) is inversely proportional to the radius of the emitter. According to Fowler-Nordheim,
\[ J = a \varphi^{-1} \beta^2 E^2 \exp \left( -\frac{b \varphi^{3/2}}{\beta E} \right) \]

In the above equation, \( a \) and \( b \) are constants that depend on the shape of the emitter.

2.2 Applications:

Field-emission cathodes are electron sources and are extensively used in vacuum devices. They are used in creating flat panel displays and in micro-propulsion systems that use thrusters that require electron sources for ion beam neutralization [2]. They are also widely used in information storage devices, mass spectrometers, and electron microscopes [3], [4].

2.3 Objectives:

As described by the Fowler-Nordheim equations, to have high current density, the field enhancement factor should be high. The field enhancement factor in turn depends on the geometry of the emitters. The relation between the applied potential \( V \) and electric field \( E \) is given by \( E = \frac{V}{r} \), where \( r \) is the radius of the surface. According to this equation, the field is highest when \( r \) is lowest. As a result, the cathodes are to be designed such that they have the lowest radius at the tips. Other factors that influence the current density are the heights of the emitters and the surface roughness [16].

In this thesis, the main objective is to fabricate high-aspect-ratio (approximately <10nm tip radius) and high-concentration cathodes that give high current densities. The goal is achieved by balancing the constraints due to fabrication steps and the geometry of the cathodes.
CHAPTER 3
NANOSPHERE LITHOGRAPHY

The first step in the fabrication of field emitters is to define a mask where the cathodes are to be etched. N-doped <111>, 2-inch silicon wafers are patterned with silicon dioxide (SiO$_2$) spheres to define the areas for etching the cathodes. These spheres are deposited using nanosphere lithography techniques where the principle of surface tension between the different materials is played to self-assemble monolayers of the silica particles on the silicon wafer.

The nanosphere lithography approach, also called as the bottom-up approach, uses small building blocks like atoms, molecules, nanoparticles, etc., to self-assemble into larger and more complex-structures. This approach is much cheaper and less time consuming compared to the other lithography techniques, like the optical lithography[19].

3.1 Self-Assembly at Air-Water Interface:

It is observed that insoluble monolayers of nanoparticles can be formed on the surface of a clean liquid with high surface tension, for example, de-ionized water. These insoluble, non-volatile particles spread at the air-water interface, if they are more attracted to water than to each other; i.e., they should possess hydrophilic head and a long hydrophobic tail [20]. This concept helps in creating monolayer films on the substrate. This technique can be best described using Langmuir-Blodgett fabrication method.
3.1.1 Langmuir Blodgett (LB) Films:

The LB fabrication method uses trough-barrier equipment to deposit monolayers of nanoparticles onto a substrate. A container made with inert material, say Teflon, that does not contaminate the aqueous subphase, is filled with the aqueous solution. The material that is to be spread is dissolved in an organic volatile solvent and dispensed on the surface of the aqueous subphase. The evaporated solvent leaves behind the nanoparticles that are trapped on the air-water interface and are spread in a monolayer fashion, which are then compressed using movable barriers that are equipped in the trough. These layers are then carefully transferred onto the substrate by vertical dipping.

3.2 Silica Deposition Technique:

In this thesis, a technique similar to Langmuir-Blodgett is developed to deposit monolayers of silica particles on the silicon wafer using a vortex-flow-enabled assembly process. In this process, initially, a silicon wafer which is somewhat hydrophilic is plasma oxidized using carbon dioxide plasma for 45 seconds to modify its surface to make it highly hydrophilic with high surface energy. A water droplet that is spread on this modified surface generates spontaneous vortex flows when a small droplet of the alcoholic solution of water, mixed in the ratio 7:5 of ethanol and de-ionized water with 40mg of silica spheres, is introduced gently though a corner of the substrate (Shown in Figure 2b and 2c). Due to the high surface energy of the substrate, the alcoholic solution rapidly spreads into a thin film, which results in the evaporation of ethanol at the fluid front owing to the Marangoni effect. Further, when the alcoholic solution encounters the already-existing water droplet, a surface tension gradient between the two liquids causes vortex flows within the droplet, thereby introducing the spheres into the droplet. Using nanospheres of appropriate size and surface functionality, trapping of the nanospheres at the air-water interface occurs as they are transported
by the vortex flows generated in the water droplet, as shown in Figure 2e. It is observed that nanospheres of low surface energies accumulate on the air-water interface, thereby reducing the interfacial surface energy of the system. Also, the vortex flows aid in compressing the trapped nanospheres to form closely packed monolayers of silica particles, which are then transferred to the wafer surface by removing the water droplet through careful and gradual tilting of the wafer (shown in Figure 2g).

Figure 2: Schematic illustration of the vortex flow-based assembly of ordered close-packed monolayers of nanospheres.
One of the several advantages of using vortex-flow assembly techniques is that large areas of uniform close-packed monolayers can be formed within few minutes. Also, it is a low-cost fabrication technique and does not need any specialized equipment like Langmuir trough to compress the nanospheres trapped at the air-water interface. Another advantage is that only small amount, as low as 5µL, of the sphere colloid can give decent areas of monolayers.

3.3 Fabrication:

Initially, large areas of monolayers are obtained by using silica spheres of 1.18µm diameter from Cospheric are added to a mixture of non-volatile solvent, which in this case is ethanol and aqueous solution, which is the de-ionized (DI) water. The solution consists of 700µL of ethanol and 500µL of DI water to which 40 mg of Si particles are added and vortexed for at least 1 minute for the particles to dissolve in the liquid phase and then sonicated for a minimum of 30 min to form a homogeneous colloid. This colloid is dispensed at a constant rate onto an n-doped <111> Si wafer using the technique mentioned in Section 3.2 and are examined under a microscope after carefully drying the moisture. Agglomerates of silica spheres and certain areas with multi-layering were noticed. These can be clearly noticed in Figure 3 as dark spots. The main reason could be that the particles were not sonicated for enough time thereby resulting in the agglomerates. To eliminate the clustered particles, the colloid is sonicated for 2 hours. Sonicating the particles for long duration did reduce the agglomerates but did not remove the agglomerates completely.
Figure 3: Assemblies formed using Cospheric 1.18µm monodisperse silica spheres mixed with 700µL of ethanol and 500µL of DI water. Some areas with agglomerates are seen in the picture at 10x magnification.

To overcome these defects and to obtain large areas of monolayers of SiO\(_2\) particles, different techniques to functionalize the surface of the particles were tested. The surface functionalization is performed such that the particles have a hydrophobic head and hydrophilic tail to ensure that the particles are trapped in a single layer at the air-water interface.

3.3.1 Surface Functionalization of Silica:

To eliminate the agglomerates seen from the assemblies when using silica particles from Cospheric, a comparative study approach was performed by using silica particles with high monodispersity and surface functionalization.
3.3.2 Particles with High Monodispersity:

Assuming, high-monodispersed silica particles could be the answer to obtain ordered assemblies, Supsil premium silica spheres of 1µm were examined. Using the same ratios of ethanol and DI water, a colloid was prepared by sonicating for 30 min. When this solution was introduced into the water surface, the particles are simply dispersed and merged into the water and did not give any assemblies. The extreme hydrophilic nature of the silica particles caused their immersion in water instead of trapping them on the air-water interface.

3.3.3 Silica with Methacrylate Termination:

To circumvent the above-mentioned situation, new silicon dioxide particles of 1µm diameter and terminated with methacrylate were chosen. The methacrylate groups are organic compounds which are derivatives of R-COOCH₃, which made the spheres hydrophobic. A colloid with these particles was prepared by adding 700µL ethanol and sonicating it for 30 min and then adding 500µL of DI water and sonicated for another 30 min. It is observed that if the DI water is added first, the methacrylate terminated silica spheres will coagulate, resulting in a non-homogeneous solution. Ordered monolayers of SiO₂ spheres could be observed on the silicon substrate using this colloid. The drawback is that the particles exhibited low mobility and did not allow the formation of close-packed layers. Also, “cracks” occur when the water surface is disturbed during the assembly process. In 2006, Shemiah M. Weeks et al., suggested that the electrostatic repulsive forces between the spheres cause stress and deform the liquid meniscus, which creates a capillary attractive force and aids the formation of close-packed assemblies [21]. As there are no proper tools to measure the surface charge density of the methacrylate terminated particles, it is only assumed but not confirmed that the surface charge density of the particles is low, thereby hindering the mobility of the particles. On smaller substrates, methacrylate-
functionalized silica showed very good assemblies compared to the larger 2-inch silicon wafers. The particles had difficulty to assemble at the farther edges. This affirms our assumption to an extent that the repulsive electrostatic forces are not strong enough to push the silica particles to the farthest end. Another reason that explains the cracks is that the parking areas and as a result the surface charge densities of the methacrylate groups are high for some particles, making them to overlap or move very close to each other and causing cracks even with the slightest disturbances in the water.

3.3.4 Surface Functionalization Using Mercaptopropyl:

The fourth method that was implemented is the surface functionalization of the silica spheres with MPTMS ((3-mercaptopropyl) trimethoxy silane). The formation of colloid through this method is a two-step process. The first step is to modify the surface of the silica spheres with MPTMS, and in the second step, the colloid is prepared with 7 parts ethanol and 5 parts DI water. Two solutions were prepared in this experiment. In the first solution, say Sol1, 40.1 mg of the monodisperse Supsil Premium, 1µm spheres are weighed and then mixed with 95% of ethanol and 5% of de-ionized water. To this, 2µL of acetic acid and 5µL of MPTMS are added and then vortexed for 1 minute. A cloudy solution forms, indicating that the particles have mixed with the solution. Now this is sonicated for a duration of 30min to ensure that all or most of the particles have reacted with the MPTMS. After sonication, the solution is centrifuged for 60 seconds at 14.5 rpm to separate the particles from the solution and then the solution is dumped, leaving the particles. The particles are then cleaned with 1000mL ETOH using the vortex and centrifuge method. Now, the colloid is prepared by adding 700µL of ETOH and 500µL of DI and then vortexed for 1 min and sonicated for 30 min. Using the same method, Sol2 is prepared, except this time the particles are sonicated twice for a duration of 30 min each, with a fresh batch of MPTMS
solution both times. The solution is centrifuged and cleaned with ethanol after the first and second 30 min runs. The longer exposure to MPTMS is done to ensure that all the silica particles are modified at the surface. Then the colloid with 7:5 of ETOH and DI is prepared and sonicated for another 30 min before using it to make assemblies.

The following observations were made between Sol1 and Sol2:

- Sol1 lost its effectiveness with time. As soon as it was prepared it gave some good assemblies, but it started to behave like Supsil Premium particles.
- The diffraction from the surface modified particles in Sol1 is like the other silica particles which is in light bluish hue.
- Sol2 gave good assemblies with time. The agglomerates were also less compared to the Cospheric particles.
- Sol2 assemblies had a diffraction different from other particles. It exhibited a bronze hue. This can be because of longer sonication time with the MPTMS, and all the particles must have been surface modified. On the other hand, Sol1 lost its effectiveness with time, as all the particles were not entirely surface modified.
- Sol1 and Sol2 gave large areas of close-packed monolayers. The microscopic images of the assemblies made using Sol1 and Sol2 are shown in Figures 4 and 5 respectively.
Figure 4: Assemblies formed from Sol1 that has been sonicated for 30 min with the MPTMS. Taken at 50x magnification.

Figure 5: Assemblies from the Sol2 which is sonicated 30 +30 min with MPTMS. Both images are at 50x magnification.

3.3.5 Particle Filtration:

Another method to reduce the agglomerates and to get uniform assemblies is to use syringe particle filters to filter the lumps from the colloidal solution that is prepared using the silica
particles. Initially the silica particles of 1.18µm diameter from Cospheric are mixed with 40ml of DI water. Then it is vortexed and sonicated until a uniform particle-water solution is formed. This is then filtered using a 3.1µm filter with glass micro-fiber membrane from Thermo Fisher Scientific. The filtered solution is then centrifuged at 3000 rpm for 2 min. The sedimented particles are then extracted carefully and later used to form the colloid. The monolayers of SiO$_2$ formed after the filtration step improved the assemblies significantly. The Figure 6 shows the top view of the monolayers of self-assembled silica spheres after the particles are filtered and 50% of the ratio of ethanol to DI water is added to form the colloid.

![Figure 6: Top view of the assemblies when seen under a microscope. The image is taken at 250x magnification.](image)

Introducing this filtration step in the colloid preparation process decreased the defects in the monolayers significantly. Another factor that played an important role in getting uniform large areas of monolayers is the quality of the silica particles themselves. It is observed that the shelf life of these particles is low and they start to show multi-layers when the same batch of the particles
is used in the long run, which could be due to the frequent opening and closing of the particle containers leading to their exposure to air.
CHAPTER 4
REACTIVE ION ETCHING

The next step in the cathode tip fabrication process is etching the silicon substrate with the self-assembled silica particles as the mask. Reactive ion etching uses ionized gas, i.e. plasma, as reactive species that etches the target material.

4.1 Etching:

Etching is a micro- and nanofabrication technique that is used to remove layers from the surface of a wafer to form the desired structures. Etching is directional and is generally referred as anisotropic etch or isotropic depending on the direction of the etch. Anisotropic etch removes material in only one direction, i.e., the etchant attacks the site of etch in only one direction, which removes the material uniformly in that direction. In the case of isotropic etch, the etchant removes the target material uniformly from all directions [19].

Etching is mainly classified into two types, namely *wet chemical etch* and *dry chemical etch*. Wet chemical etching is an etching technique which uses liquid chemical as etchants to remove the materials from the targeted wafer. During wet etching, the etchant reacts with the substrate which is usually patterned with a mask. The dry chemical etching is a technique where plasma or etchant gases are used to remove the substrate material. Plasma is partially ionized gas consisting of free electrons, ions, radicals and natural species, a fourth state of matter. The dry etching can either be physical dry etching or chemical dry etching or a combination of both called the Reactive Ion Etching (RIE). In physical dry etching, illustrated in figure 7, high-kinetic- energy
ion, electron or photon beams are incident on the targeted wafer to etch away the materials. The high-energy particles are used to knock away the atoms from the surface of the substrate, which are evaporated after leaving the surface.

Figure 7: Process showing ion bombarding the wafer during dry physical etch.

In chemical dry etching, shown in figure 8, commonly known as vapor phase etching, chemical gases attack and etch the surface of the wafer. In this method, the etchants in vapor phase chemically react with the substrate material to form compounds that are in gas phase and can be easily removed.
Figure 8: Process showing ion interaction with the substrate material in dry chemical etching.

RIE, uses both physical and chemical dry etch processes to etch away materials. This technique is widely used because it is easy to produce high-resolution structures. Also, since it is a combination of both types of etches, it is a more controlled and faster process. The physical etch helps to dissociate the substrate materials into reactive species, and the chemical etch reacts with these to form gaseous compounds.

4.2 ICP-RIE:

Plasma etch techniques are the most widely used technique in modern semiconductor fabrication. Low-pressure plasmas and low operating temperatures can achieve high selectivity and nearly perfect anisotropic etch profiles with no or minimum under-cut. To generate plasma in a laboratory environment, energy is required. This energy is provided by externally coupling electromagnetic fields with the plasma constituents. For RIE, the most commonly used techniques for generating plasmas are glow discharge plasmas (GDP), capacitive coupled plasmas (CCP), and inductively coupled plasmas (ICP).
In GDP, the plasma is generated by delivering the electromagnetic energy as a low-frequency voltage applied between a cathode and an anode. Plasma strikes when the potential difference between the conducting plates causes an initial population of the gas molecules in the chamber to ionize, which in turn collide with their neighboring molecules causing them to ionize [22]. The major drawback is that it requires relatively high voltages to initiate and sustain the plasma thereafter. This increases the energies of the ions, resulting in sputtering over the surface of the wafer rather than the smooth chemical etch that is desired. This will also lower the selectivity to the masking materials and can result in partial or full mask erosion.

In CCP, a capacitor is placed between the supplied voltage and the anode and a time-varying radio-frequency voltage is applied between the two conducting plates. Due to the RF voltage, the electrons in the plasma oscillate between the anode and the cathode, causing collisions with slowly moving massive ions, resulting in further ionizations as they transit. The capacitor between the RF supply and the anode plate results in accumulation of negative charge on the capacitor plate. The difference in potential between the plate and the anode is called the self-bias, which drives the massive positive ions towards the cathode.

In ICP technique, the supply voltage is still an RF supply, except that the electromagnetic field is generated inductively. This results in a changing magnetic field across the inductor, which induces an electric field. This field drives the massive ions towards the cathode. In this study, Oxford Plasma 100 Reactive Ion Etcher with inductively coupled plasma (ICP) coil operating at 13.56MHz at Argonne National Laboratories is used to etch the silicon wafers.
4.3 Fabrication Using RIE:

To fabricate the field emitters, the silicon wafers that were patterned previously using silica spheres are etched using RIE to form pillars. Both anisotropic and isotropic etch recipes were developed to get the desired structures. The approach was to initially etch uniform diameter pillars on the silicon substrate using anisotropic etch followed by an isotropic etch to narrow the tip diameter of the pillars.

4.4 Anisotropic Etch:

Many recipes with chlorine, CF4, CHF3 and O2 and different etch durations have been studied to get an anisotropic etch profile for the silicon. Also, the recipes were chosen such that they showed a higher selectivity towards silicon than the silica particles. Along with the gases, the recipes were explored for different inductively coupled plasma power, RF-generated forward power, chamber pressure and DC bias. Among all the recipes investigated, the recipe with chlorine gas and O2 mixture, labelled ‘Punch’, gave consistent and nice anisotropic etch profiles. Moreover, this recipe showed very good selectivity towards silicon than the silica particles with minimal etching of the spheres. The composition of gases used for the etch are shown in Table 1. Before the etching process, the RIE chamber has to be conditioned with oxygen plasma for 5 min to clean any residues from the previous etches. This step ensures that the chamber is clean prior to the etch.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cl2</th>
<th>O2</th>
<th>RF Forward Power</th>
<th>ICP Forward Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20scm</td>
<td>3scm</td>
<td>200W</td>
<td>900W</td>
</tr>
</tbody>
</table>
The recipe is tested for different time durations and the results are tabulated as shown in the Table 2. A graph of the duration of etch vs the height of etched pillars is plotted using Microsoft Excel and is shown in Figure 9. The etch rate is calculated as $0.37\mu m/min$.

Table 2: The Etch Profile of the Chlorine Punch Recipe for Different Time Durations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration</th>
<th>Pillar height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 min</td>
<td>0.47µm</td>
</tr>
<tr>
<td>2</td>
<td>3 min</td>
<td>0.84µm</td>
</tr>
<tr>
<td>3</td>
<td>4 min</td>
<td>1.05µm</td>
</tr>
<tr>
<td>4</td>
<td>5 min</td>
<td>1.21µm</td>
</tr>
<tr>
<td>5</td>
<td>6 min</td>
<td>1.76µm</td>
</tr>
</tbody>
</table>

Figure 9: Graph showing the anisotropic etch profile of the silicon pillars using the punch recipe.
The SEM image of the etch profile after 5 min of etch using the chloride punch recipe is shown in Figure 10. From the image, it can be observed that the recipe is more selective to silicon compared to the silica particles. The diameter of the spheres reduced by 0.10µm compared to silicon which has been etched to a 1.21µm in 5min. However, RIE system is observed to be highly sensitive. The etch rate of the recipe using the same parameters keeps varying with the slightest change in the system hardware.

Figure 10: Cross-sectional SEM image of the silicon wafer after 5 min of etch shows that the silica spheres have minimal etch while a significant etch can be observed on the silicon substrate.

4.5 Deep Cl₂ Etch:

To test the limits of the chloride punch recipe, the wafers are etched for several minutes with intervals of 3 min time increments. Initially, the sample is etched continuously for 6 min using the Cl₂ punch recipe with the parameters mentioned in table 1. Subsequently, the same sample is etched in increments of 3 min and imaged after every etch to observe the etch rate of both the
silicon and the silica spheres. This interval etching is continued until a point where the entire mask is etched. The SEM images are shown in the Figure 11. The first image (a) shows the etch profile after 6 min of continuous Cl\textsubscript{2} etch. The SEM image in Figure 11 (b) are the structures obtained after 6 min and an additional 3 min of etch. The depth of the pillars increased by 1.49\(\mu\)m. Continuing the etch further increased the depth of the silica pillars until the point where the silica spheres have disappeared.

4.5.1 Data Analysis, Results and Observations:

The results from the SEMs, i.e., the heights of the silicon pillars and the diameters of the silica spheres after different etch times are tabulated as shown in Table 3 and the etch rate for Si and SiO\textsubscript{2} is determined using Microsoft Excel. The graphs for the feature size vs duration of etch are plotted in Figures 12 and 13. It can be observed that the etch rates almost follow a linear trend. The etch rates of silicon is 0.531\(\mu\)m/min, and that of the Silica particles is 0.129\(\mu\)m/min. The Figure 13 shows an inverse curve as the particles are reducing in size with time. It can be observed from the images that after 15 min of interval etch, the spheres are no longer visible. There is a point between 12 min and 15 min where the mask is completely etched away.
Figure 11: Cross-sectional SEM of the sample after the deep Cl\textsubscript{2} etch. Image (a) shows structures after 6min, (b) shows 6+3min, (c) is 6+3+3min and (d) shows 6+3+3+3 min.
Table 3: Etch Profile Results Using Deep Cl$_2$ Etch

<table>
<thead>
<tr>
<th>min</th>
<th>Height of Si pillar in microns</th>
<th>SiO$_2$ diameter in µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1.18</td>
</tr>
<tr>
<td>6</td>
<td>3.19</td>
<td>0.917</td>
</tr>
<tr>
<td>9 (6+3)</td>
<td>4.68</td>
<td>0.839</td>
</tr>
<tr>
<td>12 (6+3+3)</td>
<td>7.51</td>
<td>0.587</td>
</tr>
<tr>
<td>15 (6+3+3+3)</td>
<td>9.6</td>
<td>0.20</td>
</tr>
</tbody>
</table>
It is interesting to note that from Figure 11 (d) that even though the Cl$_2$ etch is anisotropic, there is some degree of isotropic etch happening because the silica particles which act as a mask are etched gradually with time. As the etch duration increases, the silicon is etched in both the vertical and lateral directions. As a result, the pillars are smoothened and sharpened at their tops. This naturally accompanying etch is better illustrated in Figure 14.
4.6 Deep Cl\textsubscript{2} Etch Using a Patterned Cr Mask:

In this approach, an n-type silicon wafer with \textless 100\textgreater orientation is deposited with chromium film and then etched to a pattern using photolithography techniques as shown in the Figure 15.
The wafer is then deposited with silica spheres using the nanosphere lithography technique and then the Cr film is etched leaving behind the silica spheres only in the areas where there is no Cr. In Figure 15, the silica spheres are self-assembled in grey areas.

This patterned wafer is then etched using the deep chloride etch recipe and then etched for 15 min duration at a stretch. The following structures as shown in Figure 16 are obtained. The SEM images show that the tips are somewhat uniform. The tip radius is approximated to be at 138nm, which is measured by fitting a circle at the tips.

![Figure 16: SEM images of the Cr-deposited sample after 15 min of anisotropic Cl₂ etch.](image)

4.7 Isotropic Etch:

The pillars obtained from the anisotropic etch are then trimmed at the neck using isotropic etch recipe. The neck diameters of approximately 1µm are etched to form narrower necks of diameters ranging from 100-200nm. Among the various gases, SF₆ and Ar gas mixture gave good
isotropic etch profiles with narrower neck diameters and better selectivity over SiO$_2$ particles. The Table 4 shows the composition of gases and parameters used for this etch.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SF$_6$</th>
<th>Ar</th>
<th>RF Forward Power</th>
<th>ICP Forward Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20sccm</td>
<td>20sccm</td>
<td>20W</td>
<td>750W</td>
</tr>
</tbody>
</table>

The silicon isotropic etch recipe is tested for various durations to observe the etch profile and etch rate. The SEM images shown in Figure 17 show the etch profiles with hour-glass-shaped structures. The neck diameters for various etch durations are tabulated as shown in Table 5 and is plotted as shown in Figure 18. The plot shows that the etch is very non-linear. Although the 3 min 30 seconds of isotropic etch gave much narrower diameters, it did not yield consistent results and gave different etch rates for different runs. Etching for 2min 45 seconds yielded consistent results with proper cleaning and conditioning of the chamber prior to use.
Figure 17: Cross-sectional SEM images of the hour-glass-shaped structures formed after 2 min 45 sec of Si isotropic etch.

Table 5: Tabulated Results for the Neck Diameters Obtained for Various Etch Times

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration</th>
<th>Neck Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2min</td>
<td>0.45 µm</td>
</tr>
<tr>
<td>2</td>
<td>2min 45sec</td>
<td>0.251 µm</td>
</tr>
<tr>
<td>3</td>
<td>3min 30sec</td>
<td>1.51 µm</td>
</tr>
</tbody>
</table>
The major drawback with this isotropic etch recipe is that it is not always reproducible (see Figure 19). The necks break as the sample gets over-etched. The spheres are lifted off when the necks are over-etched to point where they break. Efforts were made to optimize this recipe. Prior to that, a study on the effect of process parameters on the etch rate and the effect of SF$_6$ and Ar plasmas is required.
4.7.1 Effect of Process Parameters on the Etch Rate:

The etch profile can be affected by various process parameters in the ICP system. The RIE has auxiliary radio frequency (RF) generated power and the main RF power also known as the ICP forward power. Varying both affects the etch rate and therefore the etch profile. Increase in RF power increases the electron energy which in turn increases the ionization probability [24]. Higher ionization results in increased etch rates. In addition, increased electron energy results in higher self-bias, which accelerates the ions towards the cathode with increased directionality and ion bombardment energies. This again increases the etch rate, but the selectivity is significantly decreased. Also, the high directionality of the ions improves the anisotropic etch profile.

Figure 19: SEM image of sample that has been over-etched as the silica mask is lifted off after 2min of etch.
As increased electron energies are due to the RF power, the higher plasma densities can be attained by controlling the ICP forward power. Higher plasma densities give increased etch rates and higher selectivity. As ICP power increases, the etch rate increases proportionally, reaches a maximum point, and after that starts to decreases. This trend is observed as the mean free path of the molecules is shortened [23].

Other parameters that affect the etch rate are chamber pressure, gas flow rate and substrate temperature. Lower etch rates could be noticed with increased chamber pressure and gas flow rates.

In addition to the process parameters, other factors that affect the etch rate are loading effect, where the etch rate depends on the surface area of the material to be etched. Lower etch rates are observed with increase in the amount of the etched area. Also, etch rate decreases at higher pattern density areas. Another factor is the RIE lag effect, where the etch rate decreases with decrease in feature size.

4.8 Refined Isotropic Etch:

To address the over-etch rate issues encountered in the earlier recipe, a refined isotropic etch is developed by experimenting with different gas compositions of SF$_6$ and Ar at 20W RF forward power and keeping the rest of the parameters the same. It is observed that the SF$_6$ plasma produces large quantities of atomic fluorine that quickly etches the silicon. This could be the reason behind the over-etched substrates when using 20 sccm of SF$_6$ to isotropically etch the silicon pillars [24]. The SF$_6$ reacts with silicon in the following way:

\[
4 \text{ Si} + 2\text{SF}_6 \rightarrow \text{SiS}_2 + 3\text{SiF}_4
\]
On the other hand, Argon, which is an inert gas and has heavy ions, is non-reactive with the substrate material, i.e., Si. These massive Ar ions bombard the Si surface and dislodge atoms of Si, thereby promoting the etch. Dilution of SF$_6$ with Ar boosts the electron density and therefore increases the gas activation. Therefore, controlling the individual gas to total gas composition ratio, the etch rate using isotropic etch can be controlled.

To test the theory that SF$_6$ is a more aggressive gas and is the main reason for over-etching the sample, the following series of experiments were conducted using parameters as shown in Table 6. All the samples are initially etched for 6 min using the anisotropic chloride punch recipe and then etched using the isotropic etch recipe with Ar of 20 sccm, SF$_6$ of 20 sccm and RF forward power of 20W and ICP forward power of 750W for a duration of 5 min. At this point, the samples had neck diameters at 290 nm and the heights of the pillars are at 2.7µm. The SEM of a sample is shown in Figure 20.

Table 6: Neck Diameters at Various Individual Gas Compositions and Etch Duration.

<table>
<thead>
<tr>
<th>Ar (sccm)</th>
<th>SF$_6$ (sccm)</th>
<th>Duration of etch in sec</th>
<th>Neck diameters in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>5</td>
<td>120</td>
<td>140</td>
</tr>
<tr>
<td>35</td>
<td>5</td>
<td>150</td>
<td>110</td>
</tr>
<tr>
<td>35</td>
<td>5</td>
<td>180</td>
<td>Necks are broken</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>120</td>
<td>180</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>150</td>
<td>Necks broken</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>120</td>
<td>Necks broken</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>120</td>
<td>210</td>
</tr>
</tbody>
</table>
Figure 20: SEM image showing the cross-section of the sample after 6 min of Anisotropic etch and 5 min of Cl\textsubscript{2} etch.

The Table 6 shows different etch parameters used to understand the effect of the Ar and SF\textsubscript{6} gases. The different neck diameters for various gas compositions are tabulated. It can be observed that the etch rate has increased with the increase in the gas ratio of SF\textsubscript{6}. The composition of Ar/SF\textsubscript{6} with 35sccm/5sccm and 40sccm/0sccm had a controlled etch profile compared to the other combinations. So, based on these observations, further study was done to improve the recipe. A sample is etched for 6 min with anisotropic etch recipe followed by 5 min of isotropic etch recipe. Then the refined isotropic etch recipe is used to further sharpen the necks.
The refined isotropic etch is a two-step process. In the first step, the 290nm neck diameters are sharpened by using Ar/SF$_6$ composition of 35/5 sccm for 2 min and then etched using 40/0 sccm composition for another two min. This type of etch gave an etch profile as seen in the SEM image shown in Figure 21. The neck diameters were observed to be 180nm.

Figure 21: SEM image of sample with AISO 6min, ISO of 20/20 sccm for 5 min, refined ISO of 35/5 for 2min and 40/0 of 2min.

Further etching the above sample with Ar/SF$_6$ with 40/0 sccm composition for another 2 min further narrowed the necks to 138nm as shown in Figure 22.
Figure 22: SEM image of sample with AISO 6min, ISO of 20/20 sccm for 5 min, refined ISO of 35/5 for 2min and 40/0 of 2+2min.

4.8.1 Results and Observations:

- The anisotropic etch is almost linear and does not determine the tip curvatures of the emitters. Hence, this etch recipe using chloride is reliable to produce tall silicon pillars and is unaffected by the change in etch rate due to change in the system hardware.

- However, the isotropic etch is a very sensitive recipe and has a significant role in determining the shape of the cold-field cathodes. Hence, the reproducibility of the exact same structures is not always possible with the varying system etch rates.

- It is observed that in between an RIE system maintenance cycle, etch profiles determined by the study using refined isotropic etch were nearly reproducible.
- There is a certain degree of non-uniformity observed in the etching of the silicon wafers because of the inconsistent positioning of the sample in the load lock.
CHAPTER 5
THERMAL OXIDATIVE SHARPENING

5.1 Thermal Oxidation:

Thermal oxidation is a process in which an oxidizing agent like oxygen or water vapor is forced to diffuse into the wafer at elevated temperatures. It is a chemical process to grow a thin layer of SiO\textsubscript{2} on the surface of silicon. Oxidation can be either dry or wet. In dry oxidation, the silicon wafer is settled to pure oxygen, whereas in wet oxidation, water vapor is the oxidizing agent. Dry oxides are known to give best material characteristics and quality as compared to the wet oxides.

5.2 Oxidative Sharpening of Samples:

It has been observed and documented that tips of 2-5nm are highly suitable for cold-field emission. To achieve these narrower diameters, the 250µm tips are sharpened by continuous oxidation of the pillars in the furnace. From [25], oxidation consumes silicon and during this process compressive and tensile stresses cause the side walls of the pillars at the neck merge to form a sharp tip.

Prior to placing the samples in the furnace for oxidation, the samples are dipped in a buffer oxide etch solution (diluted HF solution) for 4 min to 8 min approximately to chemically etch away the silica nanospheres. Then they are placed in a DI water bath to eliminate any further contamination of the samples and are then blow dried gently so as not to break the necks of the pillars, shown in Figure 23.
In the next step, the samples are placed in the oxidation furnace for a duration of 5.5 hours at 975°C. After 5.5 hrs of oxidation, 1700Å of oxide growth is observed. The samples are later etched using buffer oxide etch solution to remove the oxide layer and are imaged using scanning electron microscope which are shown below in Figure 24. The images show that the 5.5hrs of oxidation did not entirely sharpen the tips but looked promising.
Figure 24: Cross-sectional SEM images of the necks after 5.5hrs of oxidation at 20kx and 40kx magnification respectively. It can be observed that the necks are not completely sharpened. Image (c) is the top-view of the tips after oxidation.

To further sharpen and smoothen the tips, the samples are oxidized for another 2 hrs at 975°C and then etched again in the buffer oxide etch solution to etch away the oxide. The oxide
growth of 1080Å is observed after 2 hrs. The SEM images of the samples showed ultra-fine tips with smooth and tapered side walls as shown in Figure 25.

Figure 25: Cross-sectional (a,b,c: showing different magnifications) and top-view (d) images of the ultra-fine silicon tips obtained after a total 7.5hrs of oxidation and then etching using HF solution.
Even though the tips produced in this process are sharp and have a tip of 20nm diameter and the curvatures are approximately at 78°, the reproducibility through the etching step is not possible.

The samples etched using the refined isotropic etch were also oxidized to study the cathodes. For this, the oxidation time is calculated based on their neck diameters. The oxide growth on a flat silicon wafer can be easily predicted using Deal-Grove model, but for curved necks there is no specific mathematical calculation. So a study was done to estimate the time required for oxidizing these samples. The oxide growth and the amount of silicon consumed for different durations of oxidation on a plain silicon wafer are tabulated in Table 7.

The Silicon consumed is calculated by a simple calculation:

\[ X_{si} = X_{ox} \times \frac{N_{ox}}{N_{si}} \]

where \( N_{ox} \) is the molecular density of SiO\(_2\) and \( N_{si} \) is the atomic density of Si; \( X_{si} \) and \( X_{ox} \) are the thicknesses of silicon and the oxide respectively.

Table 7: The Oxide Growth and the Amount of Silicon Consumed for Different Durations of Oxidation on Plain Silicon Wafer

<table>
<thead>
<tr>
<th>Duration of Oxidation (hr)</th>
<th>Oxide growth (Å)</th>
<th>Si Consumed (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1080</td>
<td>49.68</td>
</tr>
<tr>
<td>5.5</td>
<td>1700</td>
<td>78.2</td>
</tr>
<tr>
<td>3.5</td>
<td>990</td>
<td>45.54</td>
</tr>
</tbody>
</table>
Since the oxide growth around the necks of the silicon pillars is slow compared to the oxide growth on flat surface [26], the time of oxidation is calculated initially by approximation and assuming that growth would be linear on a curved surface, the samples that were etched using the refined isotropic etch recipe were oxidized for 3.5 hrs. The SEM images of the samples are shown in Figure 26.

![Figure 26](image_url)

Figure 26: Image of the sample (say sample A) before and after oxidation and HF etch. The parameters used to form the structures are AISO of 6 min, ISO of 20/20sccm for 5min, refined ISO of 35/5sccm for 2 min and 40/0sccm for 2min.

From the image, after 3.5hrs of oxidation, the 180nm neck diameters are reduced to 63nm. Since the necks are visible, the sample A is further oxidized for another 2hrs, resulting in a complete removal of the necks with tip diameter at 50nm and the pillars at 1.5µm tall. Further oxidation will help reduce the tip diameters further. The SEM image is shown in Figure 27.
Similarly, Sample B, that has been etched using refined isotropic etch of 35.5sccm of 2 min and 40/0 composition for 2+2 min (i.e., a total of 4 min), is also oxidized for 3.5hrs followed by another 2 hrs. The neck diameters reduced from 138nm to 85nm after 3.5hrs and then further down to 30nm after 2hr of oxidation. The heights of the pillars are ~2µm. The SEM image is shown in Figure 28.

Figure 27: SEM image of the sample A after further 2hrs of oxidation.
5.2.1 Results and Observations:

- It is observed that the oxide growth is dependent on the orientation of the silicon wafer [27]. This could be the reason that some structures have less oxide growth compared to other structures since the crystal orientation of the pillars is changing during etching.

- The oxidation step is done only until the necks are broken. Further oxidation of samples for short durations could yield much finer tips.

5.3 Oxidative Sharpening of Deep Cl₂ Etch Samples:

The samples discussed in Chapter 4 of this thesis, where the sample is coated with a thin film of chromium and patterned using photolithography techniques, are oxidized for short intervals several times. Precisely, the sample is oxidized at 975°C for 2.5hrs thrice. This yielded much finer and smoother tips with high aspect ratios. The SEM image of these samples after the third oxidation step is shown in Figure 29.
Figure 29: SEM image of the sample that is patterned using photolithography technique.

5.3.1 Analysis:

The SEM image shown in Figure 29 has fine tips that are sharpened by several oxidation steps. The tip diameters distribution is analyzed using ImageJ software, which is a Java-enabled software and then the normal distribution curve for the tip diameters is obtained using Microsoft Excel. The tips diameters of the silicon cones are extracted from the Figure 29 and then saved into an Excel file. The mean, standard deviation, and the normal distribution are calculated as shown in Table 8. Tip diameters vs normal distribution curve is then plotted to observe the tips distribution, which is shown in Figure 30. From the graph, it can be observed that most of the tip diameters are in the range between 50nm to 120nm. These tips can be further oxidized for shorter intervals to form much finer tips.
Table 8: Table to Calculate the Normal Distribution of the Tip Diameters

<table>
<thead>
<tr>
<th>Area</th>
<th>Mean</th>
<th>Min</th>
<th>Max</th>
<th>Angle</th>
<th>Tip Diameter</th>
<th>Average</th>
<th>Standard Deviation</th>
<th>Normal Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.005</td>
<td>148</td>
<td>17</td>
<td>215</td>
<td>0</td>
<td>0.205</td>
<td>0.121</td>
<td>0.0341114932</td>
</tr>
<tr>
<td>2</td>
<td>0.005</td>
<td>179.091</td>
<td>155.15</td>
<td>221</td>
<td>0</td>
<td>0.2</td>
<td>0.121</td>
<td>0.0341114932</td>
</tr>
<tr>
<td>3</td>
<td>0.002</td>
<td>187</td>
<td>152.889</td>
<td>225.778</td>
<td>0</td>
<td>0.555</td>
<td>0.121</td>
<td>0.0341114932</td>
</tr>
<tr>
<td>4</td>
<td>0.002</td>
<td>224.074</td>
<td>213.667</td>
<td>233.953</td>
<td>0</td>
<td>0.068</td>
<td>0.121</td>
<td>0.0341114932</td>
</tr>
<tr>
<td>5</td>
<td>0.002</td>
<td>108.889</td>
<td>69.111</td>
<td>166.667</td>
<td>0</td>
<td>0.068</td>
<td>0.121</td>
<td>0.0341114932</td>
</tr>
<tr>
<td>6</td>
<td>0.002</td>
<td>106.6</td>
<td>60.333</td>
<td>151</td>
<td>0</td>
<td>0.075</td>
<td>0.121</td>
<td>0.0341114932</td>
</tr>
<tr>
<td>7</td>
<td>0.004</td>
<td>81.208</td>
<td>36</td>
<td>132</td>
<td>7.125</td>
<td>0.165</td>
<td>0.121</td>
<td>0.0341114932</td>
</tr>
<tr>
<td>8</td>
<td>0.004</td>
<td>102.444</td>
<td>64</td>
<td>200</td>
<td>0</td>
<td>0.164</td>
<td>0.121</td>
<td>0.0341114932</td>
</tr>
<tr>
<td>9</td>
<td>0.004</td>
<td>161.567</td>
<td>116</td>
<td>252</td>
<td>0</td>
<td>0.164</td>
<td>0.121</td>
<td>0.0341114932</td>
</tr>
</tbody>
</table>

Figure 30: Plot showing the normal distribution of the cathode tips.
CHAPTER 6

N-UNCD FILM DEPOSITION

Diamond, which is an allotrope of carbon, is a material with its physical and chemical properties at their extremes. Besides being the hardest material, it has high wear resistance, high thermal conductivity and chemical inertness, which makes diamond films a good material in electron field emission applications. The special properties of the diamond are due to its local bonding structure where each carbon atom is tetrahedrally coordinated with its surrounding carbon atom, which is referred as sp$^3$ bonding. The strength of these bonds is what sets the diamond films apart from other materials [28].

Microwave plasma chemical vapor deposition (MPCVD) is the most currently used diamond deposition technique. It uses plasma composed of methane (CH$_4$) and hydrogen (H$_2$) plasma to react with the surface and form methyl radicals (CH$_3$) and atomic hydrogen (H$^+$) to grow microcrystalline diamond (MCD) films. The disadvantages with MCD films is that films formed are very rough because of their large grain sizes and the use of high temperatures, typically between 700-1000ºC to grow the films, thereby limiting the variety of substrate materials on which films can be deposited [28].

However, to grow ultra-nanocrystalline diamond (UNCD) films, a novel MPCVD technique using methane plasma mixed with inert gases like Ar, Kr or Xe is used to grow the films with unique nanoscale structures with 95% of sp$^3$ bonds along with 5% of sp$^2$ and other bonds.
These bond structures have high-energy grain boundaries and as a result are much more mechanically stable.

6.1 Nitrogen-doped UNCD (N-UNCD) Deposition:

The silicon tips that have been sharpened through oxidation, when tested for field emission, wear out after a certain time. To improve the field enhancement factor, the wear resistance, total emission current and stability, silicon emitters are coated with UNCD films [10]. To make the emitters highly conductive, the tips are coated with N-UNCD films.

The deposition technique for N-UNCD films is like that of normal UNCD films except that the growth happens in CH$_4$/N$_2$ (i.e., methane/nitrogen) plasma. The substrates with the sharpened tips are initially coated with 25nm of W using sputtering technique. This W film acts as an adhesion for the diamond films and helps in preventing the substrate from getting oxidized at high temperatures during diamond growth. Also, tungsten deposition improves the seeding density of the tips when sonicated in diamond seed. These samples are initially dipped in methanol for conditioning the wafer and then sonicated for 1min in “Blueseed” and dipped in methanol and then in isopropanol. The samples are dried gently and then placed in the MPCVD chamber which is then pumped and heated to 800°C for approximately 90 min. After the chamber is completely pumped and heated and when a steady state is reached, the following gas compositions as shown in Table 9 are maintained.

<table>
<thead>
<tr>
<th>GAse</th>
<th>CH$_4$</th>
<th>O$_2$</th>
<th>H$_2$ (low)</th>
<th>Ar (high)</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sccm</td>
<td>3</td>
<td>0</td>
<td>0.4 (off)</td>
<td>160</td>
<td>40</td>
</tr>
</tbody>
</table>
Silicon cathodes that are etched for 6 min anisotropically and then 3 min 30 sec isotropically and sharpened for 7.5hrs in the oxidation chamber are used for depositing the N-UNCD films. The SEM of the sample is shown below in Figure 31. The sample had a tip radius at ~23nm. A tungsten film is sputtered for 6 min to form a 25nm film on these tips, whose scanning electron micrograph is shown in Figure 32. The N-UNCD film is then grown at a rate of 0.25µm/hr, whose SEM image is shown in Figure 33.

Figure 31: SEM image of sample (anisotropic etch 6min, isotropic etch 3min 30sec) after 7.5hrs of oxidation at 975°C show a tip curvature of 23nm.
Figure 32: SEM image of sample after 25nm of W deposition.

Figure 33: SEM image of sample after N-UNCD deposition.
6.2 Raman Spectroscopy:

Raman spectroscopy is a spectroscopic technique which is used to acquire information on the molecular vibrations and crystal structures of the materials that are being examined. It is based on the principle of Raman scattering, which was first observed experimentally by C.V. Raman in 1928 [29]. According to Raman effect, when matter is incident with light, almost all of the light is scattered. The most part of the scattered light is an elastic process called Rayleigh scattering and a small percentage of the scattering is inelastic process. Due to this, an energy difference can be observed between the scattered and the incident light. This inelastic scattered light is called the Raman scattering.

To determine the presence of diamond phase in the N-UNCD diamond films deposited, Raman spectroscopy is used. Usually, a single peak at 1332 cm\(^{-1}\) on a flat substrate implies that the given material possesses diamond phase and no other allotropes of carbon are present [30]. For a pure N-UNCD film, the Raman shift should be observed at 1300 cm\(^{-1}\) as shown in Figures 34 and 35.
Figure 34: Raman spectra of a plain silicon wafer with N-UNCD film.

Figure 35: Raman spectra of the sample with N-UNCD film.
CHAPTER 7

FIELD EMISSION TESTING

Testing the fabricated cathodes for field emission needs special vacuum chambers. The testing procedure involves examining the cathode’s robustness, their current-voltage properties and thereby determining the field enhancement factor. These fabricated samples were first mounted on a metallic cylinder and given for testing by the Physics Department, Northern Illinois University.

7.1 Experimental Setup:

The experimental setup called the DC diode test stand was used. It consists of a cathode support, a cathode mount surrounded by a cylindrical insulator and an anode as shown in the Figure 36 [31]. The prepared cathode sample is mounted on the mount using a conductive epoxy. The test setup is maintained at ultra-high-vacuum conditions of approximately \(10^{-9}\) Torr. High electric fields are applied and the current is measured using a pico-ammeter in the circuit.
7.2 FE Testing and Results:

Two types of samples are tested to ensure their field emission properties. The first sample is the one where the initial etching recipes were used to fabricate the tips. The recipe used is the anisotropic etch with chlorine for 6 min and isotropic etch with Ar and SF$_6$ of 20/20sccm composition for 2 min 45 sec. It is then oxidized for 5hrs initially and then for 2.5hrs to form fine tips. The image of this sample is shown in Figure 37. The sample is tested with applied voltages ranging from 2500V – 15KV and the current-voltage characteristics are plotted as shown in Figure 38. This sample failed after a few runs and gave a current of only 0.3nA. The field enhancement factor is also very low, 15.
The second series of tests were performed on the sample shown in Figure 36, but now coated with N-UNCD film. The SEM image of the sample coated with N-UNCD film is shown in Figure 39. With applied voltage ranges from 3KV – 6KV, the current-voltage characteristics are plotted as shown below in Figure 40. Figure 38 shows that the currents measured are in the range
of 0 - 15µA. The plot shows the data for four different runs where the voltage is systematically increased to a maximum and then lowered to a minimum. Fowler-Nordheim analysis of this data gave a field enhancement factor $\beta$ of 309 and a standard deviation of 34.

Figure 39: SEM image of the sample after N-UNCD deposition.
Figure 40: Current-voltage characteristics of the UNCD-deposited cathodes.

Comparison of the tests performed on the sample with cathodes before and after the UNCD deposition showed that the diamond coated cathodes have a higher field-enhancement factor.
CHAPTER 8

CONCLUSION AND FUTURE WORK

8.1 Conclusion:

Fabricating fine aspect-ratio cathodes with steps that include nanosphere lithography, reactive ion etching, oxidation and UNCD deposition posed many challenges. The silica assembly process is fine tuned to reduce the agglomerates by introducing the filtration step and using a fresh batch of the particles. The longer the particles are in the shelf, the more the agglomerates found in the assemblies.

The RIE process posed most of the challenges as the system is highly sensitive to changes in gas flow, pressure, temperature, and the hardware itself. The limits of the Cl₂ etch recipe to form the cathodes were studied. It is observed that the chloride punch recipe used between 12 min to 15 min would completely etch away the spheres. Even though the etch with Ar/SF₆ is inconsistent, it proved promising to obtain cathodes with high high-aspect ratios.

The oxidation samples etched with refined isotropic etch recipes delivered tips ranging between 25 to 50 nm. It is observed that the multi-step oxidation method where the structures are oxidized for 2.5hrs and then etched in buffer oxide etch solution multiple times until the tip diameters are in the sub-nm range is the most effective method. The tip diameter distribution graph shows that the sample requires additional oxidation steps to study its field emission properties.
The UNCD-coated samples that were studied for their field emission properties gave currents in the 15µA range for applied voltages of 3KV – 6KV with a field emission factor of 309. These numbers can be further improved by improving the geometry of the structures.

8.2 Comparative Study of Current Work with Previous Works:

A comparative study of the work produced in this thesis with the work contributed by Meng Ding et al. in [11], is summarized in Table 10.

<table>
<thead>
<tr>
<th>No.</th>
<th>Current Work</th>
<th>Previous Work by Meng Ding et al. [11]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fabricated using low-cost nanosphere lithography technique.</td>
<td>SiO₂ mask is grown using thermal oxidation, which is a costly and time-consuming process.</td>
</tr>
<tr>
<td>2</td>
<td>The silica mask needs no patterning as it is already patterned through self-assembly process.</td>
<td>The silica mask is patterned using photolithography technique.</td>
</tr>
<tr>
<td>3</td>
<td>The silicon underneath is etched using both anisotropic and isotropic etching techniques using Cl₂ and Ar/SF₆ plasmas.</td>
<td>The silicon is etched using just the SF₆ plasma and is etched isotropically.</td>
</tr>
<tr>
<td>4</td>
<td>Maximum of three oxidation steps were performed at high temperatures.</td>
<td>Multiple oxidation steps at low temperatures were performed.</td>
</tr>
<tr>
<td>5</td>
<td>Gate apertures were not fabricated to achieve high-concentration cathodes.</td>
<td>Gate apertures were fabricated.</td>
</tr>
<tr>
<td>6</td>
<td>Tips ranging from 20nm to 50nm were obtained with three oxidation steps.</td>
<td>With multiple oxidation steps 1nm tips were obtained.</td>
</tr>
<tr>
<td>7</td>
<td>Field enhancement factor $\beta$ obtained upon testing the cathodes is 309.</td>
<td>$\beta$ obtained is 230.</td>
</tr>
</tbody>
</table>
Future works on testing the photolithographically patterned samples and etching structures with 1nm tip diameters could yield much higher current densities. Implementing multiple oxidation steps is the key to achieving fine aspect-ratios. Another aspect that can be studied is to oxidize the samples at much lower temperatures, still working in the temperature ranges where oxidation occurs, i.e., between 850°C to 1000°C.
REFERENCES


