METAL-ASSISTED CHEMICAL ETCHING AS A DISRUPTIVE PLATFORM FOR MULTI-DIMENSIONAL SEMICONDUCTOR SCULPTING

BY

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DISSERTATION

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ABSTRACT

Conventional top-down fabrication approaches for semiconductor manufacturing can be classified into dry (anisotropic) and wet etch (isotropic or orientation-dependent) processes. At present, fabrication of novel nanostructured morphologies like porous nanowires, nanopillars with tunable aspect ratios, spiral or helical-shaped array of pits, etc. is a major bottleneck to develop novel photonic or phononic device applications which can enable a much better understanding of their underlying physics, along with demonstrating functionalities that would otherwise be impossible. The work proposed in this dissertation involves the advancement of a recently discovered top-down fabrication approach called “Metal-assisted Chemical Etching (MacEtch)” which has the potential to overcome the current limitations of 1D and 3D semiconductor nanomanufacturing processes. The main focus is on the morphology, directionality, etch mechanisms and the influence of external electromagnetic fields to engrave novel structures in both silicon and III-V compound semiconductors. The outcome of this work can lead to advancement of knowledge in the areas of propagation of light and sound waves in a nanostructured dielectric material by demonstrating novel devices using our disruptive platform for manufacturing.
To those who have faith in my potential
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TABLE OF CONTENTS

CHAPTER 1-INTRODUCTION.................................................................................................1

CHAPTER 2-MACETCH: A BRIEF HISTORY..................................................................4
  2.1 Discovery of MacEtch.............................................................................................4
  2.2 Possible Mechanism for MacEtch of Silicon.......................................................4
  2.3 Lithographic Approaches for Patterning Metal Films.........................................6
  2.4 Role of Catalyst Metals.......................................................................................10
  2.5 Role of Etchants: Type and Composition..........................................................12
  2.6 Influence of Temperature, illumination and Electromagnetic Field..................14
  2.7 Influence of Properties of Substrate.................................................................16
  2.8 Device Applications Using MacEtch....................................................................17

CHAPTER 3-MACETCH FOR 1D MICRO/NANOFABRICATION IN SILICON............19
  3.1 Demonstration of Ordered Silicon Nanopillar Arrays Using Soft-Lithography...19
  3.2 MacEtch for Tunable Aspect Ratio of 1D Nanopillars.......................................20
  3.3 Controllable Porosity of 1D Silicon Nanowires..................................................21
  3.4 Post-Doping Scheme to Mitigate Porosity Issues..............................................29
  3.5 Stability of Isolated Catalysts with Sub-Micron Feature Sizes .........................30

CHAPTER 4-MACETCH FOR 1D MICRO/NANOFABRICATION IN
COMPOUND SEMICONDUCTORS.................................................................................32
  4.1 Ordered Nanopillar Arrays in III-V Compound Semiconductors.....................32
  4.2 Demonstration of Light Emitting Diode Using III-V MacEtch.........................40

CHAPTER 5-MACETCH FOR 3D MICRO/NANOFABRICATION............................51
  5.1 Need for Magnetic-Field Assistance for 3D Microfabrication.........................51
  5.2 Demonstration of Photonic Crystal Membrane Reflectors Using h-MacEtch........52
  5.3 Magnetic-Field Assisted Drifting of Catalyst for 3D Microfabrication..............60
  5.4 Halbach Array for Planar B-Field......................................................................63
  5.5 Temperature Dependence of Magnetic-Field Assisted MacEtch......................73
  5.6 Influence of Magnetic Pulling Force on MacEtch.............................................77

CHAPTER 6-CONCLUSIONS............................................................................................94

CHAPTER 7-FUTURE DIRECTIONS..............................................................................95
  7.1 Design and Testing of Programmable h-MacEtch Apparatus............................95
  7.2 Metal Electro-Filling for Tunable Metamaterials ..............................................98

APPENDIX A-SUMMARY OF DOPING CONDITIONS USED FOR
POST-DOPING OF SILICON NANOWIRE ARRAYS......................................................99

APPENDIX B-HALF-CELL REACTIONS RESPONSIBLE FOR MACETCH
OF GALLIUM ARSENIDE.............................................................................................100
APPENDIX C-THEORETICAL CALCULATION OF SIZE OF HYDROGEN GAS BUBBLES RELEASED DURING MACETCH

APPENDIX D-CALCULATION OF MAGNETIC PRESSURE APPLIED ON IRON FILM

APPENDIX E-RECIPE FOR DRYING OF HIGH ASPECT RATIO SILICON NANOPILLARS

REFERENCES
CHAPTER 1
INTRODUCTION

Have you ever wondered what is inside a PC (or a MacBook if you are like me!), smartphone, tablet, and other electronic gadgets that surround you? To get these amazing technologies into your hands, engineers and scientists have to prepare recipes with the right choice of ingredients and tools that can handle them. Other than the commonly known materials like metals and insulators, technologists have spent several decades studying a different class of materials called “semiconductors” which can be considered as the “muscles” of these electronic gadgets. These are the materials that allow you to store, process or transfer the data received or transmitted by these technological devices. In order to train these “muscles” to get into a perfect shape based on what you want your gadgets to do for you, it is technologically essential to understand the different kinds of work-outs that can be done to tone these muscles. In the world of semiconductors, this field is called “semiconductor microfabrication” which studies the different steps and sequences that are involved in building these devices from the scratch.

Any standard textbook introducing readers to semiconductor microfabrication will have sections related to the addition, removal and definition of multiple layers on top of a substrate. Semiconductor chip and equipment manufacturers use terminologies like “deposition” or “growth” for the addition of a layer, “etching” for the removal, and “lithography” for the definition of a layer. For the removal of a layer during processing, engineers and scientists in industry and academia have always relied on two classes of etch techniques, namely, dry etch (anisotropic) and wet etch (isotropic or orientation-dependent). The choice of dry or wet etch for a given process takes several factors into consideration like etch rate, selectivity, desired aspect ratio, tolerance to damage induced during processing, cost of capital equipment and operation, etc. For several
decades, researchers working on semiconductor microfabrication have explored novel process technologies that can balance the trade-off between the dry and wet classes of etching. Metal-assisted Chemical Etching (MacEtch) is one such disruptive technology that is, in principle, a wet etch process but can produce tunable aspect ratios with minimal (or almost zero) damage to the semiconductor.

A regular wet etch process mostly uses an aggressive solution like an acid or base with some additional solvents for promoting diffusivity of etchants. In contrast, MacEtch uses an acid, an oxidizing agent and other solvents along with a thin layer of metal of suitable work function acting as the catalyst. In a wet etch process, a mask is fabricated on top of the material that must be removed and the material in contact is selectively removed by the etchants. The inherent limitation in this approach is the physical constraint on the mask that is pinned to the top surface of the material etched. This prohibits the process from achieving higher aspect ratios. In contrast, the MacEtch approach uses a metal layer which relies on a localized galvanic reaction between the metal and the semiconductor in its proximity. This approach allows extension of the etch process far from the original interface made near the top surface of the semiconductor, and thus, higher aspect ratios are possible as long as the intimate contact between the metal and semiconductor is preserved.

The entire chemical reaction behind MacEtch can be split into two half-reactions: (a) oxidation of the semiconductor and (b) dissolution of the oxidized semiconductor. The oxidizing agent used in the MacEtch solution undergoes reduction (gain of electrons) selectively on top of the metal layer (depending on the redox potential) which forces the removal of electrons (or injection of holes if you are a chemist) from the semiconductor underneath. The semiconductor in oxidized state reacts with oxygen-containing species from the oxidant and gets converted into an
oxide. The acid used in the MacEtch solution dissolves the so-formed oxide, which results in the catalyst layer moving down closer to the semiconductor surface. In this way, the process continues as long as the competition between the oxidation and dissolution steps is perfectly maintained. The choice of metal used as the catalyst is based on the Schottky barrier height at the metal-semiconductor interface and the choice of oxidant is based on the redox potential at the metal-oxidant interface [1]. With proper choice of the metal, oxidant and acid, the process window for the MacEtch of any given semiconductor can be established.

In this dissertation, we have explored the application to different semiconductor material systems with different shapes and sizes of the catalyst. In addition, we have explored the use of an external magnetic field to induce a change in the direction of motion of the catalyst during the course of the etch reaction. In Chapter 2, we have given a brief history of the process studied in this dissertation summarized from a wide range of scientific journals and review reports. Chapters 3 and 4 describe our research studies on two different types of semiconductors, that is, silicon and compound semiconductors, respectively. In Chapter 5, we have described our observations of the role of the external magnetic field that we have used to modify the process studied in the rest of the dissertation. In Chapter 6, we have presented the conclusions of all our works discussed in this dissertation. We have briefly discussed the future directions in Chapter 7.
CHAPTER 2
MACETCH: A BRIEF HISTORY

2.1 Discovery of MacEtch

One of the earliest and most widely cited work on MacEtch was reported by Li and Bohn [2], which characterized the etching of silicon with Au, Pt, or Au/Pd alloys to fabricate pores and wires. Later, several other reports started establishing the legitimacy of this process and resulted in the early foundation of this technique. A notable work by Chartier et al. [3] characterized the Ag catalyst system and discussed the relationship between MacEtch and electrochemistry of silicon. This report helped the researchers working in this field to approach MacEtch in a very systematic manner. These early reports pioneered the establishment of MacEtch and resulted in an increased acceptance within the broader scientific community. For the most recent review articles on MacEtch, the readers are pointed to the work done by Huang et al. [1] and Li [4].

2.2 Possible Mechanism for MacEtch of Silicon

MacEtch is a localized electrochemical reaction with the metal region acting as a microscopic cathode and the metal-semiconductor interface acting as the anode as shown in Figure 2.1. The oxidant used in the etching solution gets reduced locally on the surface of the catalyst where the role of the metal is to reduce the activation energy required for the reduction of the oxidant (gain of electrons). Any noble metal like Ag, Au, Pt, etc. can act as a catalyst for the reduction of an oxidant with the rate of reduction reaction directly related to the electronegativity of the metal used. The reduction of the oxidant (e.g. H₂O₂) in the presence of protonated Hydrogen (H⁺) coming from the acidic solution results in the injection of holes into the semiconductor region surrounding the metal layer. It should be noted that non-noble metals like Cr, Al, Ti, etc. cannot
act as a catalyst for MacEtch as these metals do not reduce the activation energy for the reduction of oxidants.

Figure 2.1 Schematic diagram showing the chemical process of MacEtch. The reduction of oxidant takes place only on top of the metal catalyst (cathode) and the dissolution of silicon takes place near the metal-silicon interface (anode). Hydrogen gas bubbles evolve during the course of the reaction.

At Cathode: \[ H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+ \] (Local reduction)
\[ 2H^+ \rightarrow H_2 + 2h^+ \] (Hydrogen gas formation)

At Anode: \[ Si + 6HF + 4h^+ \rightarrow H_2SiF_6 + 4H^+ \] (Dissolution of silicon)

Net reaction: \[ Si + 6HF + H_2O_2 \rightarrow H_2SiF_6 + 2H_2O + H_2 \]

In addition, there is a second cathodic reaction resulting in the formation of Hydrogen which is observed as gas bubbles during the course of the reaction. On the other hand, the injection of holes or removal of electrons from the neutral silicon atom changes the silicon from a \( \text{Si}^0 \) to a \( \text{Si}^{4+} \) state. The oxidized silicon is dissolved by HF into \( H_2SiF_6 \) which is a soluble product. Unlike wet chemical etching, the metal layer sinks to the bottom and travels along with the semiconductor which helps to achieve higher aspect ratios and novel surface morphologies. The lateral dimension of the structure formed is limited by the dimension of the metal mesh made using lithography and the vertical dimension is decided by the etch time.
2.3 Lithographic Approaches for Patterning Metal Films

The type of lithography used for MacEtch is decided based on the kind of device application that is desired for a given semiconductor structure etched. Most groups have used E-beam [5] and photolithography [6] for a large number of work reported so far. In our group, we have also used soft lithography [7] and thermal dewetting [8] techniques for a variety of different device applications. Also, the cost and throughput of a given metal patterning technique are other two strong factors that impact the choice of method used for making the catalyst. In addition, we have also explored dip-pen lithography [9] as a novel approach for metal patterning in our group. Other commonly used approaches for MacEtch include nanosphere lithography [10] and electroless deposition [11] using precursor salts containing noble metals.

In order to enable the application of MacEtch to nanostructure-based devices, it is important to be able to demonstrate a controlled fabrication of Si and Si-based. Several approaches have been reported to fabricate Si nanowire arrays with different diameters, vertically aligned non-(100) Si nanowire arrays relative to the substrate [12], Si nanowires with sub-10 nm diameter [13], as well as SiGe superlattice nanowire arrays [14]. In addition, other ordered Si nanostructures including nanopillar arrays and pore arrays have successfully been fabricated. In this section, we introduce the details of controllable fabrication of Si nanostructures using MacEtch.

2.3.1 Nanosphere Lithography

In the controlled fabrication of Si nanostructures, the salient point is the deposition of a noble metal film containing position- and size-defined pores that determine the position and size of the remaining structures after etching. The approach of Huang et al. [12] started from self-assembly of a monolayer of a Polystyrene (PS) sphere array on the Si substrate. Subsequently, the size of the PS spheres were reduced by a RIE process, transferring the close-packed PS spheres
into non-close-packed ones. In the next step, a noble metal film was deposited by thermal evaporation onto the Si substrate with the non-close-packed PS sphere as a mask. This process resulted in a continuous layer of noble metal with an ordered array of pores. The diameter of the pores was determined by the remaining diameter of the RIE-etched PS spheres. The Si substrate covered with the continuous film with pores, denoted as mesh hereafter, was etched in an etchant containing HF and H$_2$O$_2$. During the etching, the noble metal mesh sank vertically into the Si substrate. The unetched Si protruded from the etched surroundings on the mesh, exhibiting itself as a Si nanowire array.

SEM characterization shows that the average diameter of Si nanowires matches very well that of the remaining PS spheres. Using recently developed techniques in nanosphere lithography, spheres of PS or other polymers with diameters ranging from 200 nm to several micrometers are easy to assemble into highly ordered array structures on a wafer scale. Also, the technologically advanced etching processes in the semiconductor industry enable precise reduction of sphere diameter through a RIE process. As a result, the nanosphere lithography method enables control of the diameter of Si nanowires in a wide range, from ~50 nm to several micrometers. The length of Si nanowires varies linearly with the etching time, allowing easy control of their length. The upper parts of nanowires may be bent and stuck together if the Si nanowires have a relatively large aspect ratio (ratio of length to diameter) and a high areal density, and then the nanowires tend to form bundles of nanowires. The formation of bundles can be attributed to surface tension forces exerted on the nanowires during the drying of the sample, which is a common phenomenon for drying of long nanowire arrays from the solvent, and can be avoided with super-critical CO$_2$ drying.
2.3.2 Anodic Aluminum Oxide Mask

It is very challenging to assemble polymer spheres with diameters less than ~200 nm into a highly ordered monolayer array. To fabricate Si nanowires with diameters less than 20 nm, the mask must be fabricated by reducing the diameter of the polymer spheres of much larger diameter. This process generally leads to an irregular shape for the remaining polymer, and is therefore not suitable for the fabrication of Si nanowires with a well-defined circular cross-section. Furthermore, it is difficult to successfully pattern a noble metal film with arrays of discrete holes if the typical thickness of the noble metal film is comparable to the height of the size-reduced polymer spheres. For these reasons, the nanosphere lithography method is usually limited to Si nanowires with diameters larger than 50 nm. Anodic aluminum oxide (AAO) can be easily fabricated by the anodization of aluminum, which is characterized by a thin Al$_2$O$_3$ foil containing pores of diameters ranging from 10 to 350 nm with a density ranging from $5 \times 10^8$ pores per cm$^2$ to $3 \times 10^{10}$ pores per cm$^2$. Huang et al. [12] developed a method utilizing ultrathin AAO membranes as a mask to pattern a noble metal mesh, which enabled etching of a Si substrate into nanowires with diameters less than 10 nm.

2.3.3 Interference Lithography

In the fabrication of array of nanosphere and self-ordered AAO masks, defects and domain structures are inevitable. As a result, it is very difficult to fabricate defect-free Si nanowire arrays using AAO masks. The self-ordered AAO array structure is limited to hexagonal structures and usually the cross-sectional shape of Si nanowires is circular. In order to obtain Si nanowires with different array structures, different cross-sectional shape, and perfect ordering, Choi et al. [15] defined the mask using interference lithography (IL) and applied the mask to the metal-assisted chemical etching. To start with, the Si substrate was coated by a layer of ~400
nm thick photoresist. The cured photoresist was then exposed in a Lloyd’s mirror type interference lithography setup with a 325 nm wavelength laser source. The unexposed photoresist was removed by proper development, leaving behind the exposed photoresist on the substrate. Next, oxygen plasma etching was employed to reduce the size of the exposed photoresist and to remove the residual unexposed photoresist. The substrate was then subjected to a metal (Au) deposition and metal-assisted chemical etching, resulting in a perfectly ordered Si nanowire array. By adjusting the exposure process, photoresist openings with various cross-sectional shapes, including circles, ovals, and rectangles, could be fabricated. As such, Si nanowires with circular or square cross-sections or Si nanofin arrays were obtained. For a laser with a 325 nm wavelength, the density of the Si nanowire array can be tuned from $3.5 \times 10^5$ wires per mm$^2$ to $4 \times 10^6$ wires per mm$^2$. Si nanowires with a diameter of 150 nm were fabricated by this method. The approach also allows production of diperiodic structures.

2.3.4 Nanoimprinting/Soft Lithography

In our group, we used soft lithography or nanoimprinting for patterning metal films into holes or mesh-like structures for several different applications. Our approach involved transferring the patterns from a master stamp made using e-beam lithography into a PDMS stamp by mechanical pressing and baking. For a detailed understanding of the sequence of steps, the readers are referred to the work done by Prof. John Roger’s group at UIUC [16]. At the time of writing the dissertation, the method had a consistent yield with feature sizes up to ~400 nm. For smaller feature sizes, the technique had issues with opening the post on the master stamp made using e-beam lithography.
2.4 Role of Catalyst Metals

The catalyst used in MacEtch determines the rate of reduction of oxidant, H$_2$O$_2$, in the case of silicon. In general, the rate of the MacEtch process for the noble metal catalyst follows the trend Pd > Pt > Au > Ag. Also, we should note that Ag is not a stable catalyst in the MacEtch solution as it gets easily oxidized into a solution forming Ag$^+$ ions that diffuse a short distance before getting re-deposited after reduction at the HF/Si interface through the oxidation of Silicon which does not happen with Pt or Au catalysts. As the oxidant is reduced at the catalyst, holes are injected into the valence band. This charge transfer process is heavily affected by the surface bend banding of the Si at the metal catalyst contact interface. The calculations of the Schottky Barrier Height (SBH) and Potential of Valence Band Maximum (PVBM) made by Huang et al. [17] provided the first quantitative explanation of the localized galvanic etching taking place in MacEtch.

2.4.1 Type of Deposition Method

Ag, Au, Pt, and Pd are the most frequently used noble metals in metal-assisted chemical etching. Some of the commonly used methods for metal deposition on the Si substrate are thermal evaporation, sputtering, electron beam (e-beam) evaporation, electroless deposition, electrode deposition, Focused-Ion-Beam (FIB)-assisted deposition, spin-coating of particles, etc. Physical deposition in vacuum (e.g., thermal evaporation, sputtering, and e-beam evaporation) is favorable to obtain patterned structures of Si by metal-assisted chemical etching because the morphology of the resulting noble metal film can more easily be controlled in these methods. For electroless deposition, there are several different plating solutions containing noble metal ions that can be used to deposit these metals electrolessly onto a Si substrate.
2.4.2 Type of Metal

Generally, the morphologies of the etched structures vary with the type of noble metal if isolated metal particles are used for metal-assisted chemical etching. With isolated Au or Ag particles, straight pores are formed after etching into a Si substrate. But Pt particles are generally known for introducing helical pores due to the random motion of the particles during the etching, resulting in curvy pores without a uniform etching direction. In addition to morphology, the specific type of noble metal also affects the etch rate. The etch rate with Pt is much higher than that with Au. Also, the pores or wires etched into the Si substrate are usually surrounded by a porous layer with Pt, which is not as obvious with Ag or Au. One possible hypothesis for this difference in etch rate is due to the difference in catalytic activity of these noble metals for the reduction of H$_2$O$_2$ on the Si substrate. With a higher catalytic activity, more holes are injected and the possibility that the holes diffuse from the etching front to the sidewall of the etched structure increases, and thus favoring the formation of a microporous structure on the sidewall of etched structures.

2.4.3 Shape of the Metal and Distance between Metals

The shape of the metal catalyst generally defines the morphologies of the resulting etched structures as the Si under metal catalyst is etched much faster than Si without metal coverage. With well-separated noble metal particles, we usually get well-defined pores, but the etched structures might evolve from pores into wall-like or wire-like structures as the distance between noble metal particles decreases. Discontinuous patches will result in wall-like or wire-like structures with a broad distribution of cross-sectional shapes and spacing. If the metal film contains orderly distributed pores with uniform diameters and cross-sectional shapes, the Si substrate will be etched into an array of Si nanowires with identical cross-sectional shapes and spacing. Also,
the distance between metal catalyst particles or patches strongly influences the morphology of the etched structures. The nominal thickness of metal film deposited by physical vapor deposition in vacuum influences the morphologies of the etched structures. It varies with an increase in nominal thickness from isolated particles or patches to a continuous film with pores, and finally to a continuous film without pores. Thus, the different morphologies of structures from etching with metals of different thickness can be attributed to the different shapes or distances between, and packing manners of the metal particles, which are determined by the thickness of metal.

2.5 Role of Etchants: Type and Composition

The etch rate and morphology of the structures made using MacEtch are determined by the type and concentration of the etchants used. The recent review article by Huang et al. [17] provides an excellent treatment on this subject. In general, the use of higher concentration of oxidant will result in a highly porous and non-uniform etch rate due to the high probability of metal delamination due to the continuous evolution of hydrogen gas bubbles during the course of etching. Interested readers are directed to the 2012 recent report by Lianto et al. [6] on the stability of isolated catalyst disks for several different compositions of the etchants.

2.5.1 Type of Oxidant

Several different oxidants have been combined with HF to etch noble-metal-covered Si substrates, including AgNO₃, KAuCl₄ or HAuCl₄, K₂PtCl₆ or H₂PtCl₆, Fe(NO₃)₃, Ni(NO₃)₂, Mg(NO₃)₂, H₂O₂, Na₂S₂O₈, KMnO₄, K₂Cr₂O₇, O₂ bubble, or O₂ dissolved in H₂O as summarized by Huang et al. [17]. With the use of AgNO₃, KAuCl₄/HAuCl₄, or K₂PtCl₆/H₂PtCl₆, the metal ions are reduced to particles, dendrite structures, or a film depending on the etching time, parallel to the oxidation and dissolution of the Si substrate.
2.5.2 Concentration of Etchant

Both the etching rate and the morphologies of the etched structures are affected by the concentrations of H$_2$O$_2$ and HF. Chartier et al. [3] systematically studied the influence of the HF/H$_2$O$_2$ ratio on the etching rate and on the etched morphologies of Si substrates (p-(100), 1–2 Ω cm) on which isolated Ag particles were deposited by electroless plating. The morphologies of the etched structures were determined by the parameter $\rho$, defined as [HF]/ ([HF] + [H$_2$O$_2$]). With 100% > $\rho$ > 70%, Ag particles induced straight cylinder pores, the diameters of which match well those of the Ag particles at the bottom. With 70% > $\rho$ > 20%, cone-shaped pores formed. The diameter of the pore tip was the same as the diameter of the Ag particle located there, while the opening of the pore at the surface of the Si substrate had a diameter larger than that of the Ag particle. For $\rho$ below 30%, the cone-shaped pores were surrounded by micro-porous Si, which looked similar to the structure etched with Pt particles in low HF concentration. With 20% > $\rho$ > 9%, Si evolved into crater structures with opening diameters of several micrometers. With 9% > $\rho$ > 0%, neither porous nor crater structures formed and a macroscopically smooth but nanoscopically pitted surface developed.

The relationship between etching morphologies and $\rho$ was explained as follows: For 100% > $\rho$ > 70% (i.e., a high percentage of HF), the etching rate was almost completely determined by the concentration of H$_2$O$_2$ and nearly all holes generated at the Ag/Si interface at the pore tip were locally consumed because there was sufficient HF available to dissolve Si (or SiO$_x$, if this occurs as an intermediate reaction product). When $\rho$ was less than 70%, the etching rate was determined by the concentration of HF. In this case, the consumption rate of the holes at the pore tip was smaller than the generation rate. Accordingly, unconsumed excess holes could diffuse away from the tip to the sidewall of the pore. Hence, microporous Si formed on the sidewall
of the pore. With very small ρ, or very high H₂O₂ concentration, diffusion of holes was pronounced and the diffused holes appeared at every exposed surface of Si substrate. Consequently, oxidation and dissolution of Si occurred everywhere and the etching was isotropic and independent on the location of Ag particles, resulting in a polished surface.

2.6 Influence of Temperature, Illumination and Electromagnetic Field

2.6.1 Temperature

It has been shown that the length of Si nanowires made by metal-assisted chemical etching in HF/AgNO₃ solution or HF/ H₂O₂ solution increased approximately linearly with the etching time. Cheng et al. [18] systematically studied the relationship between the etching time and the lengths of Si nanowires etched at different temperatures. With a temperature in the range of 0 °C to 50 °C, a linear relationship between length of nanowire and etching time at all temperatures was confirmed. The observed etching rate increased with increasing etching temperature. From the etching rates at different temperatures, Cheng et al. [18] obtained an apparent activation energy of 0.36 eV for the formation of Si nanowires on a (100) Si substrate via the corresponding Arrhenius plot.

2.6.2 Illumination

Metal-assisted chemical etching of p-(100) and n-(100) type Si substrates with the same resistivity (1–10 Ω cm) has been conducted in the dark, with room light illumination, and with illumination from a 20 W bulb. Etching of p- and n-type substrates occurred successfully both in the dark and with illumination. For the same etching times, the difference between etching depths in the dark and with room light illumination was less than 5% for both p- and n-type substrates, while the etching depth during illumination with a 20 W bulb was about 1.5 times the etching
depth in the dark or with room light illumination, clearly demonstrating the influence of illumination on the etching rate.

The electrochemical potential of the oxidant (H$_2$O$_2$) is much more positive than the valence band of Si. Therefore, holes can be injected into the valence band of Si, independent of the doping type of the substrate. As a result, illumination is not required for metal-assisted chemical etching of an n-type Si substrate. Due to the catalytic activity of the noble metal, reduction of H$_2$O$_2$ is fast and there is sufficient number of holes injected into the Si. If the intensity of illumination is low (e.g., room light illumination), the number of photo-excited holes is much smaller than the number of holes injected from the reduction of H$_2$O$_2$, and no obvious difference in etching rate is observed. If the intensity of illumination is sufficiently high so that the concentration of photo-excited holes is comparable with or higher than the concentration of holes injected from H$_2$O$_2$, faster etching occurs.

### 2.6.3 Electromagnetic Field

Lianto et al. [6] explored the use of an external electric field to manipulate the excess holes generated during MacEtch. They placed the etchant solution in a flexible plastic container and immersed the Si sample with Au strips inside the solution. The plastic container was pressed in between two copper plates to obtain a gap between the plates of 2-3 mm. The electric field across the etching solution could then be varied by changing the potential applied (U) across the two metal plates. They found that the etch rate decreased with an increasing electric field, and this shows that either fewer holes are generated at the Au-Si interface, or fewer of the holes generated at the interface cause a reaction there. In addition, in our research group, we are exploring the use of an external magnetic field to pull a piece of ferromagnetic material (e.g. Ni or Fe) that is
sandwiched between the gold catalyst layers. Our results show that the etch rate can be manipulated with the presence of an external magnetic field.

2.7 Influence of Properties of Substrate

2.7.1 Orientation

The experiments in early years demonstrated that, indeed, in (100) and (111) substrates, the etching proceeded along the vertical direction. However, it was later revealed that non-vertical etching occurred in (111) and (110) substrates, resulting in slanting, aligned Si nanostructures. In contradiction to this, the etching of non-(100) substrates exhibited different and partly contradictory results, showing etching in the vertical direction, non-[100] directions or a switch of the etching direction from the vertical direction to one of the <100> directions. The non-vertical metal-assisted chemical etching (i.e., the anisotropic etching in certain preferred crystallographic directions) was ascribed to the back-bond breaking theory. For the oxidation or dissolution of a Si atom on the surface of a substrate, it is necessary to break the back-bonds of the surface atom that connects to the underneath atoms. The greater the back-bond strength, the more difficult it is to remove the surface atom. The number of back-bonds of a Si atom on the surface is determined by the crystallographic orientation of the substrate. Each atom on the surface of a (100) substrate has two back-bonds, while an atom on the (110) or (111) surface has three back-bonds. Due to the different back-bond strength, the Si atom on the (100) surface plane is the most easily removed, and the etching occurs preferentially along the <100> directions.

2.7.2 Doping Type and Level

Different conclusions concerning the relationship between etching rate and doping type or doping level of the Si substrate have been reported. Li et al. [2] found that under identical conditions Au-covered regions on a p+ (0.01–0.03 Ω cm) Si substrate and Au-covered regions on
a p− (1–10 Ω cm) substrate showed only small variations in pore size and etching depth, while Cruz et al. [19] reported that the etching depth in Au-covered regions of a p− (10 Ω cm) Si substrate was 1.5 times larger than that of a p+ (0.01 Ω cm) Si substrate, under identical conditions. The reason for different etching rates for substrates with different doping levels remains unclear so far. Analogous to the porous structure on the sidewall of pores in lightly doped Si substrates, it is suggested that the porous structure in highly doped Si substrates might originate from the diffusion of holes from the etching front at the Si/noble metal interface to the substrate without a noble metal during exposure to the etchant.

2.8 Device Applications Using MacEtch

Several device applications including microfluidics, SERS, capacitors, photovoltaics, thermoelectrics, LED, passive photonics, gas sensors, batteries, etc. have been demonstrated so far. Most of the earlier reports on the use of MacEtch for device applications focused on thermoelectrics, photovoltaics, batteries, etc. due to the simple and low-cost nature of the this technique. In our research group, we have demonstrated the use of MacEtch for LED [20], solar cells [21], thermoelectrics [8], and FET [22] applications. We will briefly review the results from the reports made by other research groups in this section.

Sidorenko et al. [23] explored the use of MacEtch for the fabrication of high-aspect ratio silicon nanocolumns, either attached or free-standing, and embedded into a hydrogel film and actuated them into highly controlled, complex microstructures upon contraction and/or swelling of the polymer. These architectures could be used for a variety of applications, including actuators, controlled reversible-pattern formation, microfluidics, reversible switching of the wetting behavior, tunable photonic structures, artificial muscles, and release systems. Zhang et al. [24] used MacEtch for the preparation of silver-coated silicon nanowire arrays for the creation of SERS-
active substrates which are excellent candidates for ultrasensitive molecular sensing in terms of high SERS signal enhancement ability, good stability, and reproducibility under optimal conditions. Tanaka et al. [25] used MacEtch for the demonstration of a bio-microactuator powered by vascular smooth muscle cells coupled to polymer micropillars.

Field et al. [26] and In et al. [27] used MacEtch for the fabrication of ordered, vertically aligned arrays of silicon nanowires with a porous top electrode that provide fast, low signal-to-noise ratio vapor detection. Kim et al. [28] reported the fabrication of Micro-Nano Hybrid Structures (MNHS) using a two-step silicon etching process, consisting of dry etching (DRIE or Bosch process) for micropattern formation and electroless silicon wet etching for synthesizing nanowires. By this way, they were able to create an artificial surface with microscale nucleation sites favorable for bubble generation in boiling heat transfer. Han et al. [29] reported the generic approach for constructing an air-bridged top electrical contact on extended arrays of vertically aligned nanowires made using MacEtch. While Wu et al. [30] reported the photo electrochemical characteristics of the SiNW arrays made by metal-assisted chemical etching, Huang et al. [31] reported the use of MacEtch for fabricating silicon nanowire array-based solar cells. For a more comprehensive review of the application of MacEtch for photovoltaics, refer to the review article by Li [32].
CHAPTER 3
MACETCH FOR 1D MICRO/NANOFABRICATION IN SILICON

3.1 Demonstration of Ordered Silicon Nanopillar Arrays Using Soft-Lithography

Highly doped (100) p-type wafers with resistivity in the range of 0.0005 – 0.005 Ω-cm, and n-type wafers with resistivity of 0.001-0.01 Ω-cm were used for this study. Soft lithography [16] was used to form Au mesh patterns in the size range of 200 nm – 800 nm, which results in ordered arrays of nanowires of the same diameter as the Au mesh. The lower diameter limit of the produced nanowires (200 nm in this report) is limited by the reproducibility of the gold mesh patterns produced by the soft lithography technique. A new patterning method that involves silver metal film dewetting on a silicon surface to form small Ag nanoparticles, followed by Au evaporation on such a Ag template and subsequent Ag liftoff produced an Au mesh with hole dimensions in the range 60 – 100 nm and area coverage of 30-40%.

For soft lithography patterning, a layer of SiNx was first deposited on top of the silicon wafer, followed by a spin-coated layer of SU-8. Using a PMMA stamp, the pattern was imprinted onto the SU-8. Next the depressed SU-8 was removed using an oxygen plasma etch. The sample was then subject to a CHF₃ etch to remove the exposed SiNx. The SU-8 patterns made using soft lithography were rinsed with 50:1 Buffered Oxide Etch (BOE) solution for 1 minute before evaporating metal. This step is to ensure a clean metal-semiconductor interface which is critical for MacEtch. Next, a thin layer (20 nm) of Au was deposited which was followed by metal liftoff in Piranha solution (3:1 mixture of 98% Sulphuric acid and 30% Hydrogen peroxide) for 10-15 minutes. After the metal-liftoff process, the wafers were rinsed with DI, and blown dry with nitrogen. The wafers were cleaved into samples of dimensions 1 cm *1 cm for etching. For obtaining the highly doped p-type nanowires, we varied the volumetric ratio of HF to H₂O₂ as
follows: 1:1, 2:1, 3:1, 5:1, 7:1, 10:1, 15:1, 20:1, 25:1 and 30:1. In the first set of experiments, we kept the volume of ethanol same as that of HF. In the second set of experiments, we kept a constant 10:1 ratio of [HF] to [H$_2$O$_2$] and varied the volume of ethanol from 1, 2, 3, 5, 6 and 10 parts per volume as HF. In case of highly doped n-type nanowires, we used three different volumetric ratios of HF to H$_2$O$_2$ viz. 10:1, 15:1 and 20:1 keeping the volume of ethanol as six parts per volume as HF (volumes lower than six parts had issues with metal peeling off).

3.2 MacEtch for Tunable Aspect Ratio of 1D Nanopillars

Figure 3.1 Demonstration of vertical high aspect ratio nanopillars without super critical drying. Cross-sectional SEM image of p+ nanopillars (resistivity = 0.0005-0.001 $\Omega$·cm and diameter = 550 nm) etched for (Left) 20 minutes and (Right) 40 minutes using soft lithography and [HF]/[H$_2$O$_2$]/[Ethanol] ratio of 5:1:1.

Figure 3.1 shows p+ silicon nanopillars (resistivity = 0.0005-0.001 $\Omega$·cm) of diameter 550 nm formed using the 5:1:1 recipe for 20 minutes and 40 minutes. The height ranges from 51 to 100 microns which corresponds to a change in aspect ratio of 92 to 182, respectively. All these nanopillars are vertical and highly uniform throughout the array. Chang et al. [33] reported an
aspect ratio of 220 of silicon nanowires (~20 nm diameter) subjected to Critical Point Drying (CPD) to minimize the cluttering at the tips of nanowires due to surface tension. Remarkably, the high aspect ratio nanowire arrays in Figure 3.1 were fabricated without CPD as described in Appendix E.

3.3 Controllable Porosity of 1D Si Nanowires

Figure 3.2 SEM images of p+ (resistivity = 0.001-0.01 Ω-cm) and n+ (resistivity = 0.001-0.01 Ω-cm) nanowire arrays produced by Au-MacEtch with Au mesh patterned by soft lithography. (a) to (c) 45° tilted view of p+ nanowires of 800, 550, and 200 nm in width/diameter, respectively, produced by 5:1:1 ([HF]/[H₂O₂]/[Ethanol]) recipe; (d) to (f) 45° tilted view of n+ nanowires of 800, 550, and 200 nm in width/diameter, respectively, produced by 10:1:1 recipe.

It has been shown previously that for silicon wafers with resistivity of 1 – 10 Ω-cm, the etchant concentration used in Ag-MacEtch has a significant impact on the resulting nanowire
morphology (solid vs. porous) and orientation (vertical or slanted). It was also reported that for the same MacEtch solution concentration, the porosity of silicon nanowires produced varies depending on the silicon wafer doping level; and porous silicon nanowires with a conical shape were formed for highly doped silicon using Au-MacEtch. Much different MacEtch solution concentrations are thus required to produce vertical and solid nanowires from highly doped wafers.

Figure 3.2 shows the tilted-view SEM images of highly doped p-type (resistivity = 0.001-0.01 Ω-cm) and n-type (resistivity = 0.001-0.01 Ω-cm) silicon nanowire arrays with different diameters produced by Au-MacEtch using an Au mesh pattern produced by soft lithography. The MacEtch concentrations ([HF]/[H$_2$O$_2$]/[Ethanol]) used are 5:1:1 and 10:1:1 for p+ and n+ silicon wafers, respectively. It should be noted that the 5:1:1 recipe did not lead to significant etching for n+ silicon. All but 200 nm and 550 nm diameter n+ silicon nanowires are vertical with a solid appearance under the specified magnification with these etching conditions. In contrast to the MacEtch of low-doped silicon wafers, the HF concentration needed is much higher, in other words, a lower concentration of H$_2$O$_2$ (oxidant) is required. It should also be noted that the same concentration range would lead to no pattern formation but electropolishing for low-doped silicon wafers.

To examine if the produced silicon nanowires are truly solid, we have systematically characterized the nanowires produced from p+ silicon using MacEtch solutions with [HF]: [H$_2$O$_2$] volume ratios from 3:1 to 30:1 by SEM and TEM. Figures 3.3(a)-(c) show the SEM images of highly doped (resistivity = 0.001-0.005 Ω-cm) p-type nanowires fabricated using 3:1, 7:1 and 10:1 [HF]: [H$_2$O$_2$], respectively (volume of ethanol was kept the same as the volume of HF in all cases). The high magnification SEM images of the nanowire arrays etched using 3:1 [HF]:[H$_2$O$_2$] MacEtch solutions (Figure 3.3(a)) clearly show the presence of pores. The porosity decreases with
an increasing [HF]: [H₂O₂] ratio. For concentration ratios greater than 7:1 (Figure 3.3(c)), the porosity shows significant reduction and appears to approach nearly solid morphology within the resolution of the SEM.

![SEM images](image)

**Figure 3.3** SEM images of sidewall of p+ nanowires (resistivity = 0.001-0.005 Ω-cm and diameter ~ 60-80 nm) formed with dewetting Au patterns using [HF]/[H₂O₂]/[Ethanol] recipes of (a) 3:1:3, (b) 7:1:7, and (c) 10:1:10, respectively.

However, under TEM (Figure 3.4(a)), it is apparent that pores, which appear as phase contrast in the TEM image, are still present when 10:1 MacEtch solution is used. In order to systematically study the porosity control, we record High Resolution Transmission Electron Micrographs (HRTEM) of the nanowires by tilting to [110] zone axis. We observe several regions in the interior of the nanowires where the lattice fringes are absent indicating the presence of the pores. The selected area electron diffraction (SAED) pattern confirms the single-crystalline nature of the etched wires. Further reduction of porosity has been found with continuously increasing [HF] as shown in Figures 3.4(b)-(c). The analysis of images also reveals that maximum diameter of pores reduces with the [HF]: [H₂O₂] ratio as 16 nm (7:1), 11 nm (10:1), 8 nm (20:1) and 5 nm (30:1). It is clear that the nanowires are single crystalline and the porosity at 30:1 ratio of [HF]:

23
[H₂O₂] (Figure 3.4(c)) is dramatically reduced, even though some porosity still remains in contrast to the fully solid nanowires fabricated using MacEtch from lightly doped p-type (resistivity = 10 Ω-cm) silicon wafers (Figure 3.4(d)). It should be noted that since HRTEM images are two-dimensional projections of several atomic planes of the nanowire, it is not straightforward to calculate the average level of porosity from these images.

Figure 3.4 Degree of porosity of degenerately doped p-type nanowires under different etch concentrations. p⁺ nanowires (resistivity = 0.001 to 0.005 Ω-cm and diameter ~ 60-80 nm) from dewetting pattern made using [HF]: [H₂O₂] volumetric ratio of (a) 10:1 at room temperature, (b) 20:1 at room temperature, (c) 30:1 at room temperature, and (d) shows the TEM images of solid wires made from lightly doped silicon (resistivity = 10 Ω-cm and diameter ~100 nm) for comparison. Inset shows the SAED pattern (a) from p⁺ nanowires and high-resolution TEM images (scale bar = 50 nm) of the nanowire.

The formation of high aspect ratio nanostructures with porous morphology using MacEtch has been attributed to the diffusion of holes outside of the metal-semiconductor interface and causing an additional but reduced extent of etching in the areas outside the metal mesh pattern. Hochbaum et al. [34] reported the increase in porosity of p-type silicon nanowires with increasing dopant concentration when etched under the same MacEtch concentration. Their work stated that hole transport (thus pore formation) is more favorable due to less band bending at the metal-semiconductor interface for highly doped wafers. Our experiments here provide understanding of
the role of relative concentrations of the acids and oxidants in the MacEtch solution for silicon wafers at a specific high-doping level. We hypothesize that at a very high [HF]: [H₂O₂] ratio (e.g. 30:1), the hole generation process dominates the etch rate and thus there is little time for the injected holes to diffuse before HF removal of Si⁴⁺. In other words, increasing the rate of Si⁴⁺ removal process with higher [HF]: [H₂O₂] ratio can help to reduce hole transport and thus the formation of pores. The complete model for porous silicon formation from degenerately doped wafers should include both the energy barrier model and the exact [HF]: [H₂O₂] ratio for a given crystal orientation. In our studies, we have shown the etching mechanism only for (100) silicon wafers which are degenerately doped to both p-type and n-type.

In addition to [HF], we have found that etch time also changes the porosity. Previously, Qu et al. [35] reported the increase in porosity of n⁺ nanowires made using silver-assisted chemical etching when they increased the etch time from 30 minutes to 60 minutes. Under our Au-MacEtch condition, the same trend in porosity has been found in a matter of 30 seconds vs. 60 seconds etching time using a 15:1 ([HF]:[H₂O₂]) recipe for n⁺ silicon nanowires. We have also observed a gradual change in porosity along the axis of the nanowire produced by MacEtch from these highly doped silicon wafers. In Figure 3.5, we have shown the TEM images of three segments of a nanowire produced from an n⁺ silicon wafer using [HF]: [H₂O₂] ratio of 10:1 after etching for 3 minutes. A gradual increase in porosity along the axial length (~3 microns) of the nanowire can be clearly seen. Note that this is different from the change in porosity along the axial direction by intentionally changing the [H₂O₂] during etching as reported by Chiappini et al. [36]. In our etching process, we have kept the same concentration of etchants during the entire duration. The decrease in porosity along the axis from the top to bottom of the wires may be due to the prolonged exposure of the tip and the middle parts of the wires in the etching solution. As the etching proceeds
downward, the dopant atoms inside the top and middle portions of the wires which are thermodynamically favorable sites for the formation of pores are subjected to longer exposure to etchants and hence we observe a gradual change in porosity as shown in the low- and high-resolution TEM images in Figure 3.5.

![Figure 3.5 Axial variation of porosity of n-type degenerately doped wires. Low-resolution TEM images of an n+ wire (resistivity = 0.001-0.01 Ω-cm) etched using [HF]/[H2O2]/[Ethanol] ratio of 10:1:6 for 3 minutes showing the (a) bottom, (b) middle and (c) tip regions of the nanowire. (d) to (f) show the corresponding high-resolution TEM images and the arrow indicates the etch direction. Scale bars for (a) to (c) and (d) to (f) are 50 nm and 5 nm, respectively.](image)

Not surprisingly, increasing [HF] in the solution decreases the etch rate. As shown in Figure 3.6, there is a quadratic trend in the etch depth of p+ silicon nanowires with increase in [HF] from 10, 15, 20, 25 to 30 volume by parts. All the samples were etched for a period of 10 minutes at room temperature. All SEM and TEM images from Figures 3.4 and 3.5 were obtained from nanowires of same length at approximately the same location near the top.
Figure 3.6 Variation of etch rate with chemical composition and etch time. (Left) Etch depth as a function of volume component (x) of HF for p⁺ (resistivity = 0.001 to 0.005 Ω-cm and diameter ~ 60-80 nm) nanowires etched for 10 minutes in x:1:3 ([HF]/[H₂O₂]/[Ethanol]) recipes. Etch depth decreases with higher volume components of HF (Right) Etch depth as a function of etch time for 60-80 nm p⁺ nanowires produced using 10:1:3 ([HF]/[H₂O₂]/[Ethanol]) recipe. The variation of etch depth follows a linear trend (as shown by the dashed line with arrows) after the first few minutes.

To study the etch rate dependence over time, we varied the duration of etching from 30 seconds to 15 minutes using the 10:1:3 recipe for the p⁺ nanowires made using a dewetting technique with diameters ~60-80 nm. As shown in Figure 3.6 (b), the initial etch rate is ~1 μm/min, then it increases to ~3 μm/min, as reflected by the slope of the fitted line, after approximately a minute and remains the same thereafter. We attribute this change in etch rate after the first few seconds to the presence of a thin layer of non-silicon material such as silicon suboxides (SiOₓ) formed during the metal patterning step which retards the injection of holes from the metal during the initial stage of the reaction and gradually gets dissolved by HF during the course of the reaction. We also observed the absence of any change in the color of the metal layer during the initial few seconds after dipping the sample into solution. This absence of any visible color change (an
indicator of MacEtch reaction due to diffraction from produced 3D structures) which implies a very sluggish etching process further supports the measured etch rate.

**Figure 3.7** Effect of etch temperature on porosity. Comparison of TEM images of p⁺ (resistivity = 0.001 to 0.005 Ω-cm and diameter ~60-80 nm) NWs etched using [HF]/[H₂O₂]/[Ethanol] ratio of 30:1:1 at different conditions – [(a) and (c)] room temperature and [(b) and (d)] low temperature using ice bath (0°C) with nanowire length ~3 μm. The wire boundary is also shown. The scale bars for (a) to (b) and (c) to (d) are 50 nm and 5 nm, respectively.

All MacEtch results above have been carried out at room temperature. We have found that when the etching temperature decreases, the porosity is reduced. Shown in Figures 3.7 (a) and (b) are TEM images taken from wires fabricated using the 30:1 volumetric ratio of HF and H₂O₂ at room temperature and 0 °C (ice bath), respectively. From the low resolution TEM images of the wires shown in Figure 3.7(a)-(b), we found that the nanowires made using ice bath (0 °C) has a pronounced decrease of phase contrast when compared to those made at room temperature and also had a relatively smooth sidewall morphology. We attribute this trend to the reduced rate of diffusion of injected holes into off-metal areas. The etch rate for these wires was found to be around
125-150 nanometers per minute at 0 °C which is six or seven times lower than the etch rate (800-1000 nanometers per minute) at room temperature using the same 30:1 ratio of HF and H$_2$O$_2$. Our method on low-temperature metal-assisted chemical etching of degenerately doped silicon nanowires shows a new dimension in the parameter space of controlling the porosity of nanowires. This reduction in porosity also implies that further lowering the temperature may lead to completely solid nanowires readily.

### 3.4 Post-Doping Scheme to Mitigate Porosity Issues

In order to produce silicon nanowires that had a perfect balance between sidewall roughness and electrical resistivity, we also explored alternative options for fabricating an array of wires suitable for thermoelectric device applications. In our modified process flow, we started with silicon nanowires that were made using MacEtch from lightly doped silicon nanowires with controlled sidewall roughness and performed post-doping to reduce electrical resistivity using Spin-on-Dopants (SODs) that are commercially available. The schematic diagram shown in Figure 3.8 illustrates the process integration for our approach. In this method, the silicon nanowires are capped with a thin layer of silicon oxide deposited using PECVD and the SODs are spin-coated and baked on top of this oxide layer. At the end, we seal the above two layers with another thin layer of PECVD oxide to prevent out-diffusion of dopants during the drive-in step. The thickness of the first oxide layer was adjusted to match the diffusivity of the dopants in PECVD oxide following previous reports in literature. The drive-in time and temperature were varied for silicon nanowires of different sidewall roughness and the process window was optimized by performing a two-point probe electrical resistivity of the post-doped wires by dispersing them on a different silicon chip with a thick insulating layer of PECVD oxide grown on top. The table A.1 shown in
Appendix A summarizes the electrical test results obtained from this study using two-point probe measurements.

Figure 3.8 Schematic diagram showing the post-doping scheme developed to mitigate the porosity with MacEtch of highly doped silicon nanowire arrays.

3.5 Stability of Isolated Catalysts with Sub-Micron Feature Sizes

To employ MacEtch as a silicon processing technology for applications like 3DIC, DRAM, etc. it is important to extend the feasibility of this technique to sub-micron feature sizes. Toward this goal, we have explored MacEtch at feature sizes of ~100-150 nm to etch high aspect ratio holes in silicon. Our experiments reveal that at such small scales, the concentration of oxidant used for etching plays a major role in maintaining the stability of the catalyst disks during the course of etching. With a high concentration of oxidant, the catalyst disks tend to either fly off or show lateral displacement, and thus, prohibits the etching of high aspect ratio structures.
In order to understand the influence of the Hydrogen gas bubble formation that is generally considered to be the reason for the lack of stability of the catalyst during MacEtch, we performed a systematic study of the MacEtch process under different concentrations of the oxidant. We varied the volume of Hydrogen Peroxide as 1, 5 and 20 µL while keeping a constant volume of 1 ml for the acid used. We also performed MacEtch on a control sample without any oxidant for the purpose of comparison. As shown in Figure 3.9, the stability of metal disks during MacEtch becomes significantly reduced as the volume of the oxidant is increased. This can be viewed in terms of the increase in the concentration of Hydrogen gas bubbles that get liberated during the etch process. In Appendix C, we have performed a theoretical calculation of the concentration of the gas bubbles to augment our hypothesis on the stability of the catalyst disks.

![Figure 3.9 SEM images of gold catalyst disks after MacEtch under different concentrations of H₂O₂ (shown in inset).](image)
CHAPTER 4

MACETCH FOR 1D MICRO/NANOFABRICATION IN COMPOUND SEMICONDUCTORS

4.1 Ordered Nanopillar Arrays in III-V Compound Semiconductors

Epi-ready Si-doped (100) GaAs substrates acquired from AXT, Inc. with a doping concentration of $1 - 4 \times 10^{18}$ cm$^{-3}$ were used for MacEtch. Potassium permanganate (KMnO$_4$), an oxidizing agent that has an oxidation potential lower than that of H$_2$O$_2$, was mixed with deionized water (DI) and either sulfuric acid (H$_2$SO$_4$) or hydrofluoric acid (HF). The overall etching of GaAs using KMnO$_4$ can be described by the following chemical reaction: $\text{GaAs} + \text{MnO}_4^- + \text{H}^+ \rightarrow \text{Ga}^{3+} + \text{As}^{n+} + \text{Mn}^{2+} + \text{H}_2\text{O}$, with $n$ equal to 3 or 5. The etching was carried out at either room temperature or 30 – 45°C for a period of 3 – 5 minutes as will be indicated. No stirring was done during etching. Nanoscale Au mesh patterns, with hole size ranging between 500 – 1000 nm, were prepared using a soft lithography method. First, a layer of SiN$_x$ was deposited on top of the GaAs, followed by a spin-coated layer of SU8. Using a PMMA stamp, the pattern was imprinted onto the SU8. Next, the depressed SU8 was removed using an oxygen plasma etch. The sample was then subjected to a CHF$_4$ etch to remove the exposed SiN$_x$. Following this step, a 20 nm layer of Au was evaporated on the GaAs surface. The remaining SiN$_x$ and SU8 were removed with sonication in a diluted HF solution.

Also tested were microscale square patterns of 300 µm*300 µm separated by 125 µm wide strips of gold formed with standard optical lithography using AZ5214 photoresist. SEM images were obtained using a Hitachi 4800 microscope and photoluminescence (PL) spectra were measured using a Renishaw micro-PL system with a 633 nm pump laser and a CCD detector at room temperature.
As mentioned earlier, MacEtch begins when holes \((h^+)\) that are generated from the oxidant on the metal surface and then diffuse to the semiconductor. The holes \((h^+)\) can then subsequently be consumed by oxidizing the semiconductor directly underneath the metal to form a soluble product in the acidic solution. This leads to \textit{vertical etching}. Alternatively, the holes can diffuse outside of the metal-semiconductor interface to areas around the metal to induce \textit{lateral etching}. The aspect ratio of a produced structure is inherently related to the proportion of vertical to lateral etching, which is the essence of the MacEtch mechanism. Processing factors that affect the dynamics of MacEtch can be classified into three categories: (1) semiconductor type and doping; (2) metal type, feature size, and density; and (3) solution components, concentration, temperature, and local concentration fluctuation. The focus of this study is on the third factor that limits aspect ratios, i.e. the solution. In particular, we explore the effect of oxidizing agent potential and concentration, chemical end product, accessibility to solution as a result of metal pattern size, and temperature on the etching dynamics and aspect ratio of GaAs nanostructures produced by this method.

In order to produce high aspect ratio structures, lateral etching must be suppressed. Figure 4.1 presents the effect of the oxidant concentration on the etching direction by using large size Au mesh patterns (300*300 \(\mu \text{m}^2\) separated by 125 \(\mu \text{m}\)) described in the experimental section. For metal patterns of such large size, etching takes place mostly around the edges of the metal pattern, while areas under the middle of the metal pads have limited access to solution which prevents product removal. Accumulated holes from the metal covered areas tend to diffuse laterally and side etch occurs. Figure 4.1 (a) is a schematic illustration of the typical topography produced from patterns of this size, as well as a SEM image showing the trenched profiles. The trenched etching structures are measured on two parameters; vertical etch depth and side (lateral) etch length.
Figure 4.1 Effect of oxidant concentration on vertical and side etch of GaAs using a 300*300 µm² large square mesh pattern that was subjected to a solution of KMnO₄ and HF for 3 minutes. (a) Schematic illustration of a typical etched profile defined by vertical and side etch at the pattern edges. Inset shows a SEM image of such profile. (b) Plot of vertical and size etch depth as a function of KMnO₄ concentration.

Figure 4.1(b) shows the effect of the concentration of oxidizing agent KMnO₄ on the vertical vs. side etch rate. The vertical and side etching depths are plotted using the average depth measured over multiple squares on the same sample and the standard deviation is plotted as the error bar. It can be seen that as KMnO₄ concentration increases, the vertical etch depth peaks at a concentration of 37 mM and then drops to a relatively stable value. This concentration also exhibits the best aspect ratio (vertical/side etch depth). Further increase in concentration causes the side etch to surpass the vertical etch rate, as more holes are produced at higher concentrations of KMnO₄. In order to form completely ordered structures with vertical sidewall, the dissolution step of MacEtch reaction needs to be uniform across the patterned area.

Note that patterns of hundreds of microns had to be used to evaluate side etch, and MacEtch of GaAs at the nanoscale dimensions is found to be very sensitive to all etching parameters. If the side etch is larger than the radius of the nanostructure lateral dimension, it will result in polishing with no discernable structure formation. Due to the difference in supply of holes (h⁺) for oxidation
and end product removal rate, the optimum etching recipe varies as a function metal pattern size and connectivity. For Au mesh patterns at sub-micron scales, most combinations of oxidant to acid ratio, dilution, and temperature resulted in either no etching or polishing from over etching. A suitable etching condition is determined by calibrating between the two extremes.

Figure 4.2 SEM images of high aspect ratio GaAs nanopillars produced from a 600 nm wide square Au mesh pattern in H$_2$SO$_4$ and KMnO$_4$ solution at 40 – 45 °C. (a) 30° tilted view at low magnification, (b) 30° tilted view at high magnification, and (c) side view showing the highly vertical nanopillar array.

Shown in Figure 4.2 is an array of highly vertical GaAs nanopillars produced from an Au mesh pattern with 600 nm diameter openings in a solution of H$_2$SO$_4$ over saturated with KMnO$_4$ at slightly elevated temperature for 5 minutes. The nanopillars formed are ~ 3.5 µm tall and ~ 600 nm in width. The Au mesh pattern sinks to the bottom of the pillar structure and can be seen clearly in Figure 4.2(b), just as is the case for Si MacEtch. The tips of the nanopillars appear to be tapered, probably resulting from lateral etching at the initial stage. Slight non-uniformity in the pillar width can be seen in the cross-sectional SEM image near half-height of the wire. However, the position of the narrow neck appears to be synchronized for all pillars, implying that this is due to local
etchant concentration fluctuations in the solution. Nevertheless, large area periodic arrays of ordered GaAs nanopillars are produced using MacEtch in a matter of minutes. Importantly, the solution has to be kept between 40 and 45 °C during etching. Note that using the same solution, no etching was observed at room temperature, while at temperatures higher than 45 °C, the Au pattern delaminates from the substrate surface.

![Image of periodic indentations created by inverse MacEtch using the same Au pattern as in Figure 4.2, but with Au acting as a mask in H₂SO₄ and KMnO₄ solution at 30-35 °C. (a) Side view and (b) top view SEM images with Au still on top of the surface, and (c) top view from an area with most of the Au peeled off.](image)

Interestingly, at a slightly lower temperature range of 30 – 35 °C, a metal mesh pattern of similar dimensions in the same solution etched for the same period of time acts as an etching mask for GaAs. Etching is promoted in the areas without Au coverage, yielding a GaAs grid structure with craters that have an initially sloped sidewall but a flat bottom with a depth of approximately 0.5 µm, as shown in Figure 4.3. We hypothesize that at this temperature, the etching reaction is dissolution limited. The rate determining step is the removal of the oxidized Ga³⁺ and Asⁿ⁺ (n = 3⁺ or 5⁺) into solution (e.g. Ga₃(SO₄)₃ and HAsO₂). As a result, the holes (h⁺) generated at the gold
surface are not consumed in time and instead, diffuse laterally to promote etching of the bare GaAs. Similar reverse MacEtch was reported for InP under photo-irradiation. In this case, the above bandgap photons generate electrons and holes in the bare InP area. The electrons then diffuse and recombine with the holes generated from metal catalyzed oxidant reduction in the metal covered area, causing holes to accumulate and etch the bare InP region. These results indicate that etching temperature can affect the dynamics of carrier diffusion, oxidation, and product removal, all of which are important to the spatial profile of GaAs structures generated by patterned MacEtch.

Figure 4.4 (a) Side view SEM images of an array of zigzagging GaAs nanowires at low and (b) high magnifications, formed from MacEtch using 1 µm wide square Au mesh pattern at 55.7 mM concentration of KMnO$_4$ in HF solution carried out in a glass beaker. The tips of the nanowires in (a) are clumped together due to surface tension when the wires are tall. (c) Room temperature PL spectra taken from the zigzagged GaAs nanowires, along with an unetched bulk GaAs control sample. The peaks are at 870 nm and 880 nm, respectively.

Furthermore, striking zigzagging high aspect ratio nanowires are formed by MacEtch using a solution of KMnO$_4$ and HF in a glass beaker at room temperature. Shown in Figure 4.4 is an array of wires with zigzagging sidewalls formed from a 1.0 µm diameter mesh pattern etched using 55.7 mM of KMnO$_4$ in HF for 5 minutes. From the zoomed in side image (Figure 4.4(b)), it can be seen that the zigzag pattern is synchronized horizontally. Also, the twisting direction is close to
<111> crystal orientation based on measured angles from the SEM images. It is known that MacEtch can propagate along different orientations with different etchant concentration, and high HF/oxidant ratio prefers etching along <111> directions for Si (100) substrate. We believe concentration modulation is the reason for the observed zigzagging GaAs nanowires which twist left and right from one <111> to another jointed by the straight <100> segments.

It has been reported that zigzag Si nanowires were formed using (111) Si wafers through MacEtch with the solution-based Ag catalyst AgNO₃. Notably, an intentionally scratched rough surface leads to zigzag while polished smooth surface yields straight wires. In another report, an initial porous silicon layer was deemed important for the formation of zigzag SiNWs for a Si (100) surface using patterned Au mesh as the catalyst at elevated temperature (60 °C). The porous layer acted as a barrier to deter diffusion of MacEtch reactants in the unstirred solution, creating high and low concentrations as reactants were consumed because there was a delay in replenishing them. The authors also attributed the zigzag morphology to the concentration variations [37].

In our case, intentional surface roughening did not produce zigzagging structures. However, carrying out the reaction in a glass container with HF acid was necessary, implying that the borosilicate glass container participated in the etching reaction. We hypothesize that the glass surrounding the solution is constantly turning HF into H₂O, which creates a concentration gradient that drives the diffusion of HF directly above the semiconductor wafer piece toward the container walls. In competition with the outward diffusion, HF is consumed from reacting with GaAs during MacEtch, causing the diffusion to shift back toward the wafer piece to rebalance the concentration. The constant modulation of flux during etching creates a periodic concentration variation similar to the zigzagging Si nanowire etching condition reported by Kim et al. [38]. Although the borosilicate container reaction replicated an extreme case of concentration variations during
etching, the resulting nanowire morphology clearly demonstrates the susceptibility of GaAs MacEtch to local solution fluctuations.

Figure 4.4(c) shows the PL spectrum taken from the zigzagged nanowires along with an unetched area on the same sample. A distinct shift toward a longer wavelength by ~ 9 nm relative to bulk GaAs is observed for the zigzagged nanowires, and smaller (~ 3 nm) red shift (not shown) has also been observed for the other nanowire structures formed. The red shift might be from some shallow surface states which become more important for nanowires due to the increased surface area. Further investigation is needed to elucidate the origin of this shift.

![Figure 4.5](image_url)

**Figure 4.5** Schematic illustrations (a –c) of the formation mechanism of morphologies observed in Figures 4.2 – 4.4, respectively. The etching process involves the competition of three steps: (1) hole (h+) generation from KMnO4 catalyzed by Au surface, (2) hole (h+) diffusion, and (3) oxidation and removal of etching products (Ga3+ and Asn+, where n = 3 or 5).

To summarize, Figure 4.5 shows schematic illustrations of the formation mechanism of the GaAs nanostructures reported here. Three processes labeled 1, 2, and 3 correspond to the three steps in MacEtch: hole formation, hole diffusion, and semiconductor oxidation and removal. Figure 4.5(a) corresponds to MacEtch involving H2SO4 at high temperature (40-45 °C), where the holes are removed as soon as they reach the boundary of Au, GaAs and solution. This scenario
results in high aspect ratio vertical wall nanopillars as shown in Figure 4.2. Figure 4.5(b) represents MacEtch involving H$_2$SO$_4$ at mid-temperature range (30-35 °C), where there is an excess number of holes accumulates in the bare GaAs area because the lower temperature severely reduces the rate of step 3. This mechanism leads to reverse MacEtch, as shown in Figure 4.3, where metal acts as a mask. Figure 4.5(c) illustrates the scenario of Figure 4.4, where MacEtch involves local concentration fluctuation induced by consumption and rebalance of HF/KMnO$_4$ by the borosilicate glass. The concentration modulation forces the nanowires to exhibit a zigzag morphology.

4.2 Demonstration of Light Emitting Diode Using III-V MacEtch

In the current study, GaAs (100) substrates of various doping types and concentrations were used. Semi-insulating (SI) and n-type (n = 1*10$^{18}$ cm$^{-3}$) epi-ready substrates were used as purchased (AXT, Inc.), while p-type GaAs and p-i-n GaAs samples where epitaxially grown using an atmospheric pressure Thomas Swan metalorganic chemical vapor deposition (MOCVD) reactor. For p-i-n stacked samples, a 300 nm thick un-intentionally doped GaAs layer was grown at 720 °C on epi-ready n-type substrates, followed by the growth of a 300 nm thick, heavily Zn-doped GaAs layer grown at 600 °C. The dopant concentration of the p-type samples was determined to be 1*10$^{19}$ cm$^{-3}$, based on Hall measurements.

Prior to surface patterning, all GaAs wafers were subjected to native oxide removal in dilute HCl and surface degreasing with standard solvents, followed by electron-beam evaporation of a 35 nm-thick Au film. Soft-lithography (SL) patterning was carried out by first spin-coating GaAs wafers with a thin layer of a photo curable epoxy (8% SU-8). A polydimethylsiloxane (PDMS) stamp was then pressed against the SU-8 coated substrate, followed by curing performed at 95 °C. After SL stamping, the Au-coated regions exposed through the SU-8 mask were etched using TFAC Au etchant (Transene Company, Inc.) and the overlaying SU-8 grid was dissolved in PG Remover (MicroChem Corp.). This resulted in a square-grid-patterned Au layer on the GaAs
substrate, where the exposed GaAs windows are ~ 1*1 µm² separated by a spacing of ~ 550 nm. The current approach improves upon our previously reported SL patterning method for GaAs by ensuring a pristine Au/GaAs interface, thereby guaranteeing uniform MacEtch over the entire patterned areas.

MacEtch was performed in a solution containing potassium permanganate (KMnO₄) as the oxidant, and hydrofluoric acid (HF) as the source for removal of the oxidized material, and de-ionized water (DI). Oxidant concentration was varied such that the mass of KMnO₄ in the etching solution was tuned within the range of 0.025 – 0.20 g. Acid dilution levels were modified within an HF:DI volumetric ratio range of 5:1 to 1:5 at a constant total volume of 30 ml in all etch tests. This corresponds to a HF: KMnO₄ molar ratio of 0.14 M: 7.9 µM to 0.70 M: 1.6 µM. All etch durations were fixed at 10 min., unless otherwise stated. LED fabrication was carried out by first selectively etching the Au layer from the as-etched p-i-n GaAs samples, followed by spin-coating of an SU-8-2 resist layer. A 150 s oxygen-plasma RIE procedure allowed for the planarization of the SU-8-2 layer and the exposure of the MacEtched nanopillar tips. Next, a 250 nm thick indium-tin-oxide (ITO) layer was sputtered on the exposed nanopillar tips as a transparent and conductive contact layer, followed by partial coverage with an electron-beam evaporated Au top contact of 500 nm thickness, situated around the active pillar array. The backside of the n-type GaAs substrate was contacted by a Ni/Au (5 nm/500 nm) stack. Finally, the fabricated devices were subjected to a 30 s rapid thermal annealing (RTA) procedure for the formation of Ohmic contacts.

Inspection of the MacEtched nanopillars and general imaging was carried out using a Hitachi S-4800 scanning electron microscope (SEM). All PL and EL experiments were performed at room temperature using a Renishaw inVia micro-PL system, equipped with a CCD camera. For PL experiments, excitation was provided by a 633 nm HeNe pump laser source. In EL experiments,
the laser source was shuttered and the devices were operated in continuous mode as power was supplied by an Agilent E3649A DC source in a two-point probe configuration.

Figure 4.6 Tilted view SEM image of a p-GaAs sample after MacEtch in a solution of 15 ml HF, 15 ml DI, and 0.025 g KMnO₄. The inset shows a higher magnification view of the same sample (scale bar represents a 1 µm length). The sidewall roughness exhibited in the inset results from the direct projection of the Au layer edge roughness.

A tilted-view SEM image obtained from a p-GaAs sample subjected to MacEtch in a solution of 15 ml HF, 15 ml DI, and 0.025 g KMnO₄ is shown in Figure 4.6, with the inset showing a high-magnification view of the same sample. The square-shaped nanopillars are 1.8 µm tall and roughly 1 µm wide laterally (aspect ratio of 1.8), as predefined by the soft-lithography mask employed. The continuous Au catalyst layer can be observed at the base of the pillars, characteristic of the MacEtch mechanism as previously described in Section 2.2 under Chapter 2. Note that the vertical grooves on the sidewalls of the pillars are the direct consequence of the edge roughness of the Au pattern, which are faithfully engraved onto the sidewalls of the GaAs pillars. We believe the metal edge roughness is a result of the Au liftoff step during SL patterning,
Figure 4.7 Quantification of VER as a function of (a) solution temperature, (b) acid dilution ratio, and (c) oxidant concentration. Etch rates for p-, i-, and n-GaAs samples are represented by red circles, black squares, and blue triangles, respectively. Each data point represents mean VER values obtained from samples sets of 25 nanopillars (with vertical sidewall structures), while error bars represent ± one standard deviation from the mean.

where wet etching of the polycrystalline Au film likely attacks the grain boundaries preferentially, leaving a saw-tooth edge pattern. In contrast, much smoother sidewalls were produced by MacEtch
using evaporated Au patterns, although the drawback of this patterning method is the risk of leaving organic resist residues between Au and the GaAs surface. In the current approach, direct patterning of the Au layer allows for more reproducible and uniform MacEtch over large (wafer-scale) areas.

First, the dependence of vertical etch rate (VER) is studied as a function of etching temperature. Figure 4.7(a) quantifies this trend, based on p-, i-, and n-type GaAs samples MacEtched in a common solution consisting of 15 ml HF, 15 ml DI, and 0.05 g KMnO₄. All data points represent measurements obtained from sample populations consisting of 25 nanopillars, while the error bars represent one standard deviation (some error bars may not be distinguished, as they represent values smaller than the extent of the data points). A clear linear progression in vertical MacEtch rate is noted with increasing temperature, from 0 to 40 °C, beyond which the VER saturates. This trend, as previously observed in the case of Si MacEtch, is attributed to increased thermal promotion of $h^+$ diffusion through the catalyst layer and enhanced mass transport of dissociated ions. Importantly, this demonstrates for the first time that room temperature MacEtch of high aspect ratio nanopillars can be achieved for all doping types of GaAs. While the etch rates of n- and i-type GaAs remain comparable, p-type samples etched under identical conditions exhibit a higher VER by a factor of roughly 2.3 at room temperature. The fact that doping type changes the etch rate with identical Au pattern feature sizes indicates that charge transport, instead of mass transport, is the rate determining factor. It has been reported that the Schottky barrier height, which can be affected by the metal work function, thickness, and size, as well as the semiconductor doping type and level, can affect the etch rate, with faster etch rates for n-type GaN and thicker Au for p-type Si[39]. The Schottky barrier height analysis used in the case of GaN cannot explain the doping type dependence observed in the current study, possibly because
the etching condition that is low in oxidant concentration makes the majority carrier transport in
the semiconductor play a dominant role in determining the etch rate. Although the exact nature of
this VER enhancement has not been explored in the current study, we believe it is related to the
inherent excess presence of holes in p-type samples and, therefore, improved oxidation
rates. Under the conditions described above, room-temperature MacEtch proceeds with a VER of
318 ± 9 nm/min, 132 ± 6 nm/min, and 141 ± 8 nm/min for p-, i-, and n-type GaAs, respectively,
with negligible lateral etching.

Next, the effect of acid dilution on VERs is considered. Figure 4.7(b) shows the VER as a
function of the HF:DI ratio, resulting from room-temperature etching at a constant oxidant
concentration of 0.05 g. Figure 7(b) demonstrates that the optimal (highest) VER is realized for a
volumetric acid dilution ratio of 2:1. For a fixed total solvent volume, increasing the acid content
is associated with a higher rate of dissolution of oxidized material. However, below a critical
dilution level (2:1 in the current case), the etch rate is dramatically reduced. This highlights the
significance of the role of DI as a surfactant in III-V MacEtch. Thus, DI serves to reduce the
surface tension between the acid and the semiconductor surface and allows for the acid to access
the oxidized material. Similar trends in VER with acid dilution were observed for all three GaAs
doping types. Optimal VERs of 474 ± 16 nm/min, 159 ± 7 nm/min, and 177 ± 18 nm/min were
measured for p-, i-, and n-type GaAs, respectively.

Lastly, the influence of oxidant concentration on VER is considered, as plotted in Figure
7(c). In this room-temperature MacEtch experiment, optimal HF and DI volumes of 20 ml and 10
ml, respectively, were employed, while KMnO₄ concentrations were varied from 0.025-0.2 g. As
anticipated from previous GaAs MacEtch experiments, VER increases monotonically with oxidant
concentration. It should be noted that in the current study, the maximum KMnO₄ concentration
employed is equal to the minimum level of what had previously been reported for GaAs MacEtch. Reducing oxidant levels minimizes the risk of porosity in the nanopillar sidewalls. The p-type samples again exhibit accelerated etch rates, by a factor of $2.6 \pm 0.3$, in comparison to n- and i-type samples for all oxidant concentrations.

Figure 4.8 Tilted view SEM images demonstrating nanopillar morphology control. (a) Sample etched in a solution of 10 ml of HF, 20 ml of DI, and 0.1 g of KMnO$_4$ for 30 min. (b) Sample etched in a two-step process: first in the same solution as (a) for 10 min, followed by 3.5 min in a solution of 20 ml of HF, 10 ml of DI, and 0.1 g of KMnO$_4$ where lateral etching is quenched.

The lateral etch rate (LER) of GaAs nanopillars may also be tuned as a function of the MacEtch solution, by decreasing acid content and increasing oxidant concentrations. Figure 4.8(a) shows an SEM image of a nanopillar array etched for 30 minutes at room temperature in a solution consisting
of 10 ml of HF, 20 ml of DI, and 0.1 g of KMnO₄. While the MacEtched nanopillars shown in Figure 4.6 adopted the exact dimensions (pillar widths of 1 µm) of the Au-catalyst mesh layer, those shown in Figure 4.8(a) clearly show a distinct lateral width reduction (aspect ratio of ~ 7.3). In the latter case, the use of an etching solution consisting of higher oxidant and lower acid concentrations allows for enhanced \( h^+ \) generation and, when not consumed immediately, the holes diffuse, thereby promoting the oxidation of material further from the Au/GaAs interface. By successively reintroducing nanopillar samples to distinct MacEtch solutions, each tuned to specific VERs and LERs, nanopillar morphologies can be engineered. Figure 4.8(b) shows a sample that has been etched in two steps, first in the same high LER solution described above for a period of 10 minutes, followed by a second 3.5 minutes etch in a solution consisting of 20 ml of HF, 10 ml of DI, and 0.1 g of KMnO₄. In this case, GaAs pillars (aspect ratio of ~ 2.5) are formed with tapered tips, consistent with an enhanced LER profile, and square base segments, consistent with a MacEtch scheme where lateral etching is effectively suppressed. This demonstrates a key advantage of the MacEtch process, as standard RIE methods do not allow for such morphological tuning and independent control of the lateral profile to generate 3D hierarchical structures.

Room temperature PL spectra acquired from three distinct p-i-n GaAs MacEtched samples are compared with a PL spectrum obtained from a planar p-i-n GaAs sample in Figure 4.9. The red, blue, and green curves correspond to samples shown in Figures 4.6, 4.8(a) and 4.8(b), respectively, while the black curve corresponds to a planar control sample, which was not subjected to MacEtch. Whereas all spectra demonstrate a broad peak with center wavelength of 876 nm, associated with band-to-band radiative recombination in GaAs, the PL emission intensity is strongly correlated to nanopillar morphology. Specifically, by increasing the volume of the exposed GaAs nanopillars, photon escape probabilities and, thus, PL intensities are increased. It
should be noted that comparison of room temperature PL spectra obtained from MacEtch- and ICP-RIE-fabricated p-i-n GaAs pillar arrays of similar dimensions shows a small (~10 %) intensity difference, in favor of the MacEtched sample. This further demonstrates that MacEtch may indeed serve as a competitive process to conventional RIE techniques for such applications. The optical quality of MacEtched structures may surpass those produced by RIE as the pillar size becomes smaller and surfaces play a bigger role.

Room temperature EL spectra obtained from both nanopillar arrays (thick, solid curves) and planar (thin, dashed curves) p-i-n GaAs LED samples are shown in Figure 4.10(a) at varying levels of current injection. The inset to Figure 10(a) shows a cross-sectional SEM image of a LED fabricated from MacEtch produced p-i-n GaAs nanopillars arrays, according to the processing scheme described above, after a 7.5 minutes MacEtch process in a solution of 20 ml HF, 10 ml DI, and 0.1 g KMnO₄. This results in the formation of 2.2 μm tall nanopillars with base and tip widths...
of approximately 800 nm and 600 nm, respectively. The top ITO layer is formed such that only the p-GaAs segment is contacted. Figure 4.10(b) plots the EL intensity as a function of the current injection for both the nanopillar array (red) and the planar control (black) samples. The most notable feature is that EL intensity from the nanopillar samples exceeds that of the planar sample at all comparable current levels (as also indicated by the EL spectra). Larger enhancement is observed with an increasing injection current, implying better current spreading with the pillar structure, analogous to the micro-pixel LED geometry. It should be noted that improved current spreading in such geometries should also yield greater internal quantum efficiencies at high injection current densities. Beyond 225 mA (equivalent current density of 1.4 A/cm²), where intensity saturation was first noted, the EL intensity from the MacEtched nanopillar array exceeds

Figure 4.10 (a) Room temperature EL spectra obtained from planar p-i-n GaAs control sample LEDs (thin, dashed curves) and MacEtched nanopillar p-i-n GaAs LEDs (thick, solid curves) at various current levels. The inset shows a cross-sectional SEM image showing LED device structure with superimposed device schematic. (b) Plot of EL intensity as a function of injected current for both samples.
the intensity measured from the planar stack by a factor of roughly three. Note that no surface passivation is employed for the pillar-based LED sample. With more surface area introduced due to the pillar structure, lower emission efficiency would have been expected if surface related non-radiative recombination dominated, as was the case for micro InGaN LEDs where RIE was used for mesa formation. The fact that intensity degradation is not observed in the current study implies that MacEtch does not cause detrimental damage to the sidewalls. Additionally, we attribute this enhanced efficiency to the light extraction improvement from the nanopillar array, allowing for more efficient photon escape as well as multiple scattering interactions, which reduce the probability of photon re-absorption. The LED performance is expected to greatly improve by optimizing the pillar size, spacing, and height, as well as applying surface passivation and better metal contact schemes. A broader impact of this work relates to overcoming the “efficiency droop” phenomenon by employing damage-free, high aspect ratio pillar-based LED designs in a wide range of compound semiconductors, particularly in InGaN green LEDs.
CHAPTER 5
MACETCH FOR 3D MICRO/NANOFABRICATION

5.1 Need for Magnetic-Field Assistance for 3D Microfabrication

A few groups have reported the MacEtch of randomly distributed holes in bulk Si using metal nanoparticles formed by electroless deposition, [40]–[42] which limits the use of this approach only to applications where a periodic arrangement of holes is not required. However, for the formation of Photonic Crystals (PhCs) and metamaterials, uniform etching of an array of holes of sub-micron scale dimensions with precisely defined lattice configurations is critical. Unlike the formation of vertical pillars using a metal mesh layer as the catalyst, drilling an array of holes using isolated catalysts is more challenging due to the absence of connectivity and, thus, coherence while descending between neighboring metal disks. This necessitates the modification of conventional MacEtch methods reported to date to be used for the drilling of holes in Si and other semiconductor materials with controlled lattice configurations.

In 2012, Oh et al. [43] reported the direction-guided, nano/micro shaping of Si using an applied magnetic field for intentionally changing the direction of motion of the catalyst during MacEtch, resulting in the formation of sheets, needles, and zigzag wires. This work motivated us to explore magnetic field-guided MacEtch (h-MacEtch) to overcome the challenges in using isolated metal catalysts for the formation of periodic arrays of holes. Such a field-guided MacEtch process can lead to the formation of straight air hole arrays with high aspect ratios, and curved air holes with controlled chirality, a process that is otherwise unachievable with conventional dry etching. In this section, we report a systematic study of the etch parameters required for the fabrication of periodic nanohole arrays of sub-micron dimensions on silicon-on-insulator (SOI) wafers using MacEtch under the influence of an external magnetic field. We then demonstrate, for
the first time, the fabrication of high-performance two-dimensional (2D) air hole array PhC Si membrane reflectors (Si-MRs) using this approach.

5.2 Demonstration of Photonic Crystal Membrane Reflectors Using $h$-MacEtch

Figure 5.1 (a) 3D sketch of a Si-MR with a patterned 2D air hole square-lattice PhC structure on an SOI substrate. (b) Key lattice parameters for the square-lattice air hole PhC structures are air hole radius ($r$), lattice constant or period ($a$), and Si-MR thickness ($t$). (c) 45° tilted-view SEM image of a nanohole array after a 60 s magnet-guided MacEtch process showing trilayer metal stacks displaced to the bottom of the etched Si air holes. Inset shows a tilted-view image of a single drilled nanohole and the catalyst disk after MacEtch. Inset scale bar represents 500 nm.

As shown schematically in Figure 5.1(a), a square-lattice air hole PhC structure on an SOI substrate was used for our design. The key lattice parameters are shown in Figure 5.1(b), where $r$, $a$, and $t$ represent air hole radius, lattice constant (period), and Si-MR thickness, respectively.
The design was based on rigorous coupled-wave analysis (RCWA) techniques [44], [45]. For the PhC Si-MR design considered here, with target reflection spectral band around 1500 nm, the design parameters are \( a = 980 \) nm, \( r/a = 0.28 \), and \( t = 340 \) nm.

After defining the patterns using electron-beam lithography (EBL), we deposited a trilayer stack of metals—Au (20 nm)/Ni (10 nm)/Au (5 nm)—on an SOI wafer—2 \( \mu \)m buried oxide (BOX) and 340 nm top Si—using electron-beam evaporation followed by liftoff to form metal disk patterns. The typical sample size was \( \sim 0.5 \) mm*0.5 mm. We then introduced the SOI wafer with metal disk patterns into a Teflon beaker with 49% hydrofluoric acid (HF, 5 ml), 30% hydrogen peroxide (\( \text{H}_2\text{O}_2 \), 1.25 ml) and deionized water (DI, 8 ml) for different etch periods (specified below). A stack of circular Neodymium magnetic disks (Applied Magnets), with maximum measured magnetic field strength of 0.2 T, were placed underneath the beaker containing the MacEtch solution to ensure uniform and vertical drilling of holes in the active device area, by avoiding the detouring of metal catalyst disks during etching. The distance between the top surface of the magnet and the SOI wafer was \( \sim 5 \) mm. Following MacEtch, the SOI wafers were submerged into a commercial gold etchant (Transene Co.) to completely remove the metal stack. Imaging and general inspection of post-MacEtch samples were carried out using a Hitachi S-4800 scanning electron microscope (SEM). For optical reflectivity measurements, a white light source (covering 1100-1700 nm spectral range) and an optical spectrum analyzer were used to measure the reflection spectra over a wide spectral bandwidth.

Figure 5.1(c) shows a tilted-view SEM image of a nanohole array (diameter = 550 nm and pitch = 1 \( \mu \)m) fabricated on a p-type (\( \rho = 5-10 \) \( \Omega \)-cm) Si wafer using a 60 s MacEtch process under the influence of an externally applied magnetic field. During the course of etching, the trilayer metal disks sink vertically into the substrate (as shown in the inset) due to the influence of the
applied magnetic field attracting the central Ni layer of the trilayer metal stack in a downward
direction. By varying the duration of etching, this approach allows for the drilling of vertical holes
of any aspect ratio, so long as a perfect interface between the catalyst disk and the underlying
semiconductor substrate is preserved. In addition, by switching the polarity and duration of the
applied external magnetic field, this technique may, in principle, be extended to drilling helical or
spiral-shaped pits for 3D photonic device applications, [46] which cannot be achieved by other
anisotropic etching processes. It should be noted that the edge roughness of the metal disk controls
the smoothness of the nanohole sidewalls, due to the inherent nature of the MacEtch process [47].

For the fabrication of PhCs in Si, the technique used should produce uniform and vertical etching
of holes of any given lateral and vertical dimensions. Therefore, we designed a set of experiments
varying the magnetic field strength, duration of etching, and lateral dimensions of holes, in order
to determine their influence on the MacEtch process.

As Oh et al. reported that the applied magnetic field controls the direction of motion of the
catalysts [43], we compared the morphology of holes made using MacEtch with and without an
external magnetic field. In Figure 5.2(a), the nanohole array fabricated using MacEtch without an
applied magnetic field clearly shows the non-vertical sinking of catalyst disks into Si, whereas the
nanoholes etched with an applied magnetic field of 0.2 T, as shown in Figure 5.2(b), demonstrates
a significant reduction in non-vertical displacement of disks. We also observed that with field
strengths less than 0.2 T (not shown here), there were still signs of lateral detouring. This can likely
be attributed to the lack of a sufficiently localized field strength near the etch front, thereby causing
the displacement of the disks. Also, we note a clear enhancement of the vertical etch rate with the
introduction of a 0.2 T magnetic field, as seen in Figure 5.2(b). This is a direct consequence of
the additional attractive magnetic force induced upon the Ni segment of the metallic trilayer stack.
Figure 5.2 45° tilted-view SEM images of nanohole arrays after MacEtch for 60 s with (a) zero and, (b) 0.2 T external magnetic field guidance. The scale bars represent 5 μm.

Very recently, Lai et al. reported the mechanics of catalyst motion during MacEtch of Si by studying the van der Waals (vdW) force between the catalyst and Si during etching and its dependence on the chemistry of the solution [48]. The detouring observed in our MacEtch experiments without the applied magnetic field (Figure 5.2(a)) can be attributed to the non-uniform and anisotropic nature of this vdW force, even with our optimized etching conditions having a high [HF]:[H₂O₂] ratio. The enhancement of etch rate with the application of an external magnetic field (Figure 5.2(b)) can be attributed to the manipulation of both the magnitude and direction of the same attractive vdW force, which is very similar to the observations of enhanced etch rates,
reported by Lai et al. [48], with increasing molar concentrations of HF and H$_2$O$_2$. Therefore, with the application of a sufficiently high external magnetic field (in this case, 0.2 T) and etch duration, our MacEtch approach can produce vertical holes of variable aspect ratios in Si.

![Figure 5.3 Plots showing variation of etch depth with (a) duration of MacEtch and (b) diameter of holes under identical etch conditions. Each data point represents the mean value measured from a sample set of 25 individual nanoholes, while error bars indicate ± one standard deviation from the mean.](image)

The second influential parameter of interest is the duration of MacEtch. Figure 5.3(a) shows the variation of etch depth as a function of etch time for nanohole arrays of 550 nm diameter and 1 µm period, made using p-type Si wafers under a constant magnetic field (0.2 T). A nearly
linear trend is observed from Figure 5.3(a), indicating that the vertical etch rate of such discrete features is constant. It is worth noting that a slightly lower etch rate is observed for shorter etch periods, likely the result of a latency period required for substantial oxidation of Si. These results demonstrate that tuning of the aspect ratio of such vertical nanoholes, simply by varying the etch time, can be achieved with the proper choice of magnetic field strength.

Lastly, we consider the effect of variation of the nanohole lateral dimensions on the etch depth, for a fixed MacEtch duration and constant magnetic field. The diameter of the holes used for our study ranged between 400 to 1000 nm, as this range corresponds to the sub-wavelength regime used for the design of PhC-based devices. All samples were etched under a constant external magnetic field of 0.2 T for a fixed duration of 60 seconds. As shown in Figure 5.3(b), the etch depth of nanoholes decreases as the diameter of the holes increases using a constant pitch of 1 µm for all the samples. This decrease in etch rate can be attributed to the difference in the number of Si atoms undergoing oxidation during the MacEtch process with different lateral dimensions of the metal patterns. For etching holes in the sub-400 nm regime (not shown here), much higher etch rates can be expected as the number of Si atoms would be reduced even further. Therefore, the current MacEtch approach may be easily scaled down to implement such design requirements.

For the SOI wafer used for our optical reflectivity measurements, we set the etch duration as 75 seconds in order to ensure full penetration of the catalyst disks through the top Si layer (t = 340 nm). In Figure 5.4(a), the top view SEM image of a Si-MR formed on top of the BOX layer is shown. We observed that when the metal catalyst reaches the underlying BOX layer, MacEtch no longer continues, as etching of this segment proceeds isotropically in HF (no Si layers are present in the BOX to be oxidized). The patterned MRs formed using MacEtch can be released from the SOI substrate by selectively etching the BOX layer in HF, as shown in Figure 5.4(b), and
can be directly transferred to any other substrates based on the transfer printing technique [49].

Note that

![SEM image of Si-MR](image)

**Figure 5.4** (a) Top-view SEM image of a Si-MR made from an SOI wafer using magnetic field-guided MacEtch for 75s, and (b) 45° tilted-view SEM image of a Si-MR released from the SOI wafer with an alternative lattice configuration (~ 1 µm hole size with 2 µm period). The MRs shown in the tilted-view SEM image in Figure 5.4(b) had a square air hole with an alternative lattice configuration (~ 1 µm hole size with 2 µm period).

Figure 5.5 shows the measured (solid, red curve) and simulated (dashed, blue curve) optical reflectivity spectra from a MR with a MacEtch-patterned 2D air hole square-lattice PhC structure. The parameters used for simulation to fit the experimental results are $a = 980$ nm, $r/a = 0.313$, and $t = 340$ nm. Notice that the fitted $r/a$ value is slightly larger than the original design parameter, due to enlarged air hole sizes in the actual etched structures. Clearly, the key features in the broad high-reflection band region between the experimental and simulated optical reflectivity results match very well. The measured peak value of reflectivity is approximately 90% of the simulated value at the desired wavelength of 1500 nm. Note that the Si-MR fabricated using the $h$-MacEtch approach reported here has a slightly reduced peak reflectivity compared to the Si-MRs made using the dry etch approach reported earlier [50] with similar design parameters. This could be attributed to the
*h*-MacEtch conditions used here, that is limited by the metal edge roughness resulting from the patterning approach and the uniformity of the magnetic field. Further improvement of the reflectivity can be achieved by minimizing the sidewall roughness and size dispersion of the etched nanoholes. Under fully optimized condition, it is possible that the reflectivity of the device can

![Figure 5.5](image.png)

**Figure 5.5** Comparison of optical reflectivity data obtained by RCWA simulations (dashed, blue curve) and experimental measurements (solid, red curve) of the Si-MR fabricated by magnetic field-guided MacEtch.

surpass that produced by dry etch, because of the inherent damage-free nature of MacEtch. The results demonstrated here confirmed experimentally for the first time that MacEtch, a simple, low-cost, and damage-free technique, can be used for the fabrication of Si-MRs without the need for high vacuum conditions or a high thermal budget, as required for conventional plasma-assisted etching. Most importantly, the work reported here demonstrates the feasibility of the *h*-MacEtch
process for fabricating high-quality photonic structures, where more complicated 3D structures may be realized in the future.

5.3 Magnetic-Field Assisted Drifting of Catalyst for 3D Microfabrication

5.3.1 Experimental Setup for Demonstrating Magnetic-Field Assisted Drifting during MacEtch

In our initial demonstration of the planar B-field as shown in Figure 5.6, we used a vertical stack of permanent magnets (N48 grade) that we bought from commercial vendors. The stacks were placed on either side of the Teflon beaker containing the MacEtch solution such that the magnetic field in the region in between the two stacks has opposite polarities. We also measured the variation in the magnetic field strength as we move from one edge to another, and the values ranged from 500 to 2500 Gauss as shown in Figure 5.6. We defined the field pointing perpendicular to the surface as Z direction, and the field parallel to the surface and pointing from North to South Pole as X direction. In order to switch between Z and X direction, we manually moved the Teflon beaker from a configuration with a vertical stack of magnets providing a Z directional magnetic field to the configuration for X directional field that is described in this section. Also, we made sure the samples are placed near the circumference of the Teflon beaker in order to make use of the highest value of magnetic field that is generated along the X direction.

Also, in order to study the effect of thickness of the ferromagnetic material on the enhancement in etch rate during magnetic-field assisted MacEtch, we performed a systematic study of MacEtch of holes in silicon using dot patterns of ~1 µm diameter and ~3 µm pitch following an identical ratio of acid and oxidant for all the experiments. We noticed that the etch depth achieved obtained after a given etch duration under different values of thickness of metals like Ni and Fe keeps on increasing with the increase in the thickness of the ferromagnetic metal. Also, the samples having Fe as the ferromagnetic material (shown in red) shows a higher etch
depth when compared to the samples etched with Ni as the middle layer. This trend could be related to the magnetic permeability of the type of the ferromagnetic material that is used for the MacEtch experiment. Also, we noticed that the middle layer (both Fe and Ni) gets attacked by the acid used in the etch solution which limited us to perform this study only up to a thickness of 100 nm beyond which we started to see the top and bottom layers of Au getting completely separated due to the complete removal of the middle layer.

Figure 5.6 Apparatus for h-MacEtch using permanent magnets. (Left) Photographic image of the magnetic configuration using a stack of Neodymium-based permanent magnets stacked on both sides of the MacEtch solution with the direction and magnitude of field generated and (Right) effect of thickness of ferromagnetic layer on the etch rate of h-MacEtch process.

As a follow-up to our construction of our apparatus, we performed MacEtch experiments along the two different directions following different sequences. In the image shown in Figure 5.7, we used a circular dot pattern with a diameter of ~4 microns made using photolithography and performed etching by using a volumetric ratio of HF, H₂O₂ and ethanol as 5:2.5:5. In our first attempt, we performed a three-step process in a Z-X-Z sequence by moving the Teflon beaker between the two different configurations for magnetic field for a duration of 15 minutes for each
step. We noticed that the circular disks sink along the vertical direction during the first 15 minutes, and then show a drift along the X direction due to the pulling force acting along the parallel direction from the stacks placed on the sides. It should be noted that the drifting of the dots is not happening at the same rate as compared to the sinking rate along the vertical direction following identical etch conditions. We attribute this difference in rates due to the lack of symmetry in the shape of the circular catalyst disks which has a preference to etch along the Z direction due to the

![Image of 3D semiconductor sculpting](image)

Figure 5.7 A 3D semiconductor sculpting using permanent magnet-based h-MacEtch. Cross-sectional SEM image of holes etched in silicon using permanent magnet-assisted h-MacEtch and 5:2.5:5 volumetric ratio of HF, H₂O₂ and ethanol (a) with a three-step process (Z-X-Z) by moving the magnets from the bottom (Z direction) to the side (X direction) of the beaker for a duration of 15 minutes for each step and catalyst disks of diameter ~4 µm, (b) with a two-step process (Z-X) for 15 minutes each and catalyst disks of diameter ~0.6 µm, and (c) with a two-step process (X-Z) for 15 minutes each and catalyst disks of diameter ~4 µm. The magnetic fields used for Z and X directions were 1800 Gauss and 2500 Gauss, respectively. Scale bars for (a), (b), and (c) are 5, 1, and 10 µm, respectively.

availability of larger area with Au-Si interface, and hence, more probability for oxidation and dissolution of Si atoms. Also, we tested smaller dot patterns with a diameter of ~0.6 micron as shown in Figure 5.7(b), and noticed that the dots are able to drift a relatively larger distance under this case along the X direction following an identical etch recipe. A closer look at the trial left by
the circular dot patterns also reveal the bending of the catalyst disk with a raised portion in the inner region implying that the circular disks are bending downwards during the course of etching. The stress acting on the trilayer metal stack (Au/Ni/Au) could be the reason for this bending of the catalyst which provides more stability of the catalyst during the course of the drifting along the X direction.

Also, the increase in the distance of drifting along the X direction could be correlated to the decrease in the diameter of the circular disks as compared to the previous case. In addition, we also performed a reverse sequence in which we started with the X directional drift and then proceeded to the Z directional etch to verify whether the previous observations can be done in an opposite fashion. We noticed that the circular disks follow the X directional drift for the first 15 minutes and started etching along the Z direction during the second sequence, and thus, confirms the reversibility of this multi-directional etching technology. In all our experiments, we used a magnetic field of 1800 Gauss along the Z direction, and 2500 Gauss along the X direction.

5.4 Halbach Array for Planar B-Field

![Halbach Array Image]

Figure 5.8 Photographic image of a Halbach array. This consists of 12 wedges, all producing fields that collectively sum to approximately 1 T in the center bore. The dimensions are 4.31 cm OD*1.27 cm ID*2.54 cm thickness. In this picture, the field inside the bore points upward.
With the stack of permanent magnets described in Section 5.3, a major drawback with the design is the lack of uniformity of the magnetic field intensity near the surface of the sample undergoing MacEtch. In order to overcome this drawback, we explored a different configuration called “Halbach array” to achieve a uniform magnetic field along the X direction. Basically, the Halbach array is a set of permanent magnets (12 pieces in our case) stacked together such that the polarities of the individual segments in the array are arranged in such a way that there is a constructive summing up of individual field strengths only in the air gap in the middle of the array, and zero or almost negligible field strength in the region outside. In Figure 5.8, we have shown a photographic image of the Halbach array that we bought from our vendor (Gaussboys). The setup used has 12 wedges which collectively sum to produce a magnetic field of approximately 1 T in the center bore. The current design of the Halbach array has an inner diameter of about an inch which restricts the maximum size of the Teflon beaker that we can insert in the center bore. In all our experiments, we used a Si chip that can fit into the middle of the Halbach array. This is again a limitation with the current design for generating a magnetic field along the X direction. Also, in our MacEtch experiments, we used two different Halbach arrays that can generate a magnetic field of 0.16 T and 1 T in the middle of the air core. We also ensured that the samples undergoing etching along the X direction were kept along the direction where the field points from North to South to induce the trilayer catalyst stack to drift from one end to another in a controlled fashion.

5.4.1 Circular Dot Patterns

In order to calibrate the Halbach array for our magnetic-field assisted MacEtch experiments, we preformed MacEtch of circular dot patterns of diameter ~0.6 µm with a trilayer stack of catalyst—Au (20 nm)/Fe (10 nm)/Au (20 nm)—with and without an external magnetic
field. In the control sample that was etched without an external magnetic field, we noticed that the circular disks showed a lot of non-vertical sinking as the etch process started from the top as shown in the cross-sectional SEM images in Figure 5.9. This could be attributed to the lack of stability of the gold catalyst disk during the course of etching. However, when we etched the same sample

![Cross-sectional SEM images](image)

**Figure 5.9** Testing of Halbach array with lower magnetic field. Cross-sectional SEM image of sample etched for 30 minutes using a HF:H₂O₂:IPA volumetric ratio of 20:10:32 (a) without an external magnetic field, and (b) with the Halbach array of 0.16 T with the direction of magnetic field pointing right to left.
with the circular Halbach array having a B-field of 0.16 T in the middle of the air gap, we noticed an angled etch morphology where the disks showed a uniform drift toward the left with an inclination of ~156° with respect to the normal to the surface. In terms of the etch depth, the samples etched with the Halbach array had a slightly higher value which could be attributed to the presence of an external magnetic field that is trying to induce the catalyst disk to follow a restricted path during MacEtch. Also, the inclined nature of the pits etched into Si also indicates that the shape and symmetry of the catalyst disks play a significant role in inducing a non-vertical etch direction with this approach. Given the planar and cylindrical nature of the trilayer stack of metals in this study, we can only expect a dragging effect along the X-direction, and thus, the angle of inclination may not be brought down anywhere closer to 90°.

However, with the same approach, if we could replace the trilayer stack of metals with a spherical structure having a core and shell of ferromagnetic and catalytic metal layers respectively as shown in Figure 5.10, we could expect the etching to happen in a much more precisely controlled manner.

![Figure 5.10](image)

**Figure 5.10 Need for symmetrical catalyst for 3D h-MacEtch.** Schematic diagram illustrating the need to replace the currently used 2D stack of trilayer catalyst to a spherical core-shell architecture with better encapsulation of Fe layer and symmetrical shape for better control of motion of catalyst during field-assisted MacEtch.
5.4.2 Star-Shaped Disks

In addition to the circular dot patterns, we also tried star-shaped disks as shown in Figure 5.11 which have an inner core diameter of ~1 micron and four symmetrical arms of widths ~0.5 micron. With the application of an external magnetic field of 1200 Gauss along the vertical direction, the star-shaped disk patterns show a vertical etching resulting in vertical pits of depth ~425 nm after 20 minutes with the MacEtch recipe corresponding to \( \rho = 90^{16.7} \) reported by Hildreth et al. [51]. It should be noted that the star-shaped disks show a vertical etch depth of ~425 nm unlike the spiraling effect observed by Hildreth et al. [51] that used a larger feature size and without any external magnetic field. We hypothesize that the external magnetic field acting along the vertical direction is forcing the catalyst arms to sink in a vertical direction without causing any rotational effect due to the pressure differential acting on the arms of the catalyst.

![Image of star-shaped catalyst disks](image-url)
Figure 5.12 Star-shaped catalyst disks for calibrating circular Halbach array. (a) and (b) A 45° tilted-view SEM image of star-shaped disk pattern made on Si after MacEtch with a vertical magnetic field of 1200 Gauss for 20 minutes followed by etching for another 10 minutes using the circular Halbach array with a field of 1600 Gauss. Inset shows the top-view SEM image of the spiral pit formed with the two-step etch process.

In contrast, as shown in Figure 5.12, when we performed a two-step etch process where we repeated the Z directional etch mentioned above as the first step, followed by X directional etch using a circular Halbach array for another 10 minutes, we observed that the star-shaped disks are forming spiral-shaped pits with the rotational effect starting after the initial vertical etch profile of ~425 nm corresponding to the first step. This rotational effect with the introduction of the circular Halbach array is a new phenomenon that has not been reported yet by any other research groups. It is recommended that we perform a systematic study of this rotational effect using the circular Halbach array to understand the physics behind the deformation of catalyst arms and develop a predictive model to etch spiral pits with different geometrical parameters.
5.4.3 Current Challenges with Multi-Dimensional Semiconductor Sculpting

In order to test the possibility of multi-directional etching using the current configuration of permanent magnets, we performed a set of experiments related to magnetic-field assisted MacEtch. In our first attempt, we tried a four-step process using a MacEtch recipe of 5 ml of HF, 0.5 ml of H₂O₂ and 4 ml of DI at room temperature. For the Z directional etching, we used a vertical stack of magnets producing 0.35 T near the surface, and for the X directional etching, we used a circular Halbach array producing a B-field of 1 T in the middle. The samples had a trilayer stack of catalyst—Au (10 nm)/Fe (10 nm)/Au (10 nm)—on a lightly doped Si. Our sequence of changing the directionality is as follows:

1. Z directional etch for 10 minutes
2. X directional etch for 5 minutes with the field pointing from North to South
3. Z directional etch for 10 minutes
4. X directional etch for 5 minutes with the field pointing from South to North

Our SEM images in Figure 5.13 show that the four-step process did not result in a zig-zag structure which was our goal. Instead, we observed that the catalyst disk shows a hinging effect (shown with white arrows) in the middle of the etch pits. It should be noted that all the neighboring catalyst disks showed the same drift away from the pit at the same depth from the top surface. We hypothesize this lateral drifting to the effect of the planar magnetic field acting on the catalyst during the second step using the circular Halbach array which tries to attract the ferromagnetic layer toward one end during the course of MacEtch. However, since the iron layer is relatively thin, there is not enough surface area with Au-Si interface along the direction of the magnetic field, and thus, the disks are showing a hinging effect instead of a longer drifting along the X direction.
Figure 5.13 Demonstration of multi-directional etching inside a silicon via with high aspect ratio. (a-c) 45° tilted-view SEM images of pits etched into Si using our four-step multi-directional etching using magnetic-field assisted MacEtch.

In order to improve the outcome of this experiment, it is worth repeating the same four-step process with a core-shell architecture-based system which should have more symmetry in shape of catalyst, and hence, more probability for longer etch length along the X direction. It should also be noted that the catalyst disks prefer to move in a vertical path that is slightly tilted from the normal to the plane of the wafer when we repeated the Z directional etching in our third sequence. We attribute this to the lack of planarity of the catalyst disks after the X directional drift with the circular Halbach array used in step 2. Our current observations also do not reveal much information about the minimum requirements for the external magnetic field strength that is required for each of the steps used in our sequence. In the future, it would be worth attempting the same experiment with several different field strengths in order to gain a better understanding of the catalyst deformation that is happening after the X-directional etching attempted here.
In our second attempt, we performed MacEtch on an array of circular dot patterns using the same recipe used in our earlier attempt for a duration of 30 minutes. The dots showed a vertical sinking and the etching was shallow as shown in the top-view SEM images in Figure 5.14.

We also performed the same experiment using the circular Halbach array with the polarity of the field facing North to South as we moved from left to right with respect to the surface of the sample.
As shown in Figure 5.15, we can clearly see a preferential drift of the catalyst disks toward the right matching the direction of the field inside the central air gap. This experiment demonstrates the intentional motion of the MacEtch catalyst along the direction of the external magnetic field. It should be noted that the disks are showing only a smaller drift length of less than a micron even after etching for 30 minutes. Also, the catalyst disks are showing drifting along several different directions along the top surface of the Si chip. Even with the application of a very high field of 1 T, we have not been able to demonstrate the drifting along a specific direction. This is a serious issue with the current design of our experiments. In the future, if we can repeat the same experiment with a spherical catalyst with a core-shell architecture, it would increase the controllability of this process.

![Top-view SEM images of holes etched in Si with HF: H₂O₂: DI volumetric ratio of 5:0.5:4 following a two-step process with Z directional etch for 10 minutes and X directional etch for 5 minutes.](image)

Figure 5.16 Top-view SEM images of holes etched in Si with HF: H₂O₂: DI volumetric ratio of 5:0.5:4 following a two-step process with Z directional etch for 10 minutes and X directional etch for 5 minutes.

In addition, we also performed a two-step etch process, wherein we etched the sample along the Z direction for 10 minutes, followed by etching along the X direction for 5 minutes to
get a better understanding. We noticed that the disks are showing a tunnel-digging effect with the disk going deeper during the first step etched along the Z direction and starts drifting along the surface during the etching along the X direction as shown in Figure 5.16. Also, we noticed that the disks with a larger diameter of ~0.9 µm show a very shallow tunnel whereas the disks with a smaller diameter of ~0.5 µm show a deeper tunnel with the disks trying to pop-out of the plane of the wafer after drifting for a while underneath the plane of the wafer.

5.5 Temperature Dependence of Magnetic-Field Assisted MacEtch

The objective of this task was to understand the relationship between the energy barrier for the MacEtch process and the magnitude of the external magnetic field intensity used for guidance. By performing magnetic-field assisted MacEtch under different temperatures, we can generate an Arrhenius plot for the rate of the MacEtch process. From the slope of this plot, we can extract the

Figure 5.17 (Left) Top-view SEM image of stretched mesh pattern used for the temperature-dependence study and (Right) a single pillar etched inside the mesh pattern after 15 minutes of MacEtch at room temperature.
activation energy for the MacEtch rate of formation. We prepared a micron-scale mesh pattern with extensions on all four edges as shown in Figure 5.17 for the purpose of this study. The mesh patterns were subjected to a magnetic-field assisted MacEtch process using a mixture of 20 ml of HF, 5 ml of H₂O₂, 4 ml of IPA and 4 ml DI with an external magnetic field intensity of 0.22 T. The temperature of the MacEtch bath was varied from 20 to 50 °C in increments of 5 °C using a hot plate. The temperature of the water bath used for heating the MacEtch solution was monitored frequently using a lab thermometer to maintain a stable temperature during the course of MacEtch. For this purpose, we used a short duration of 30 minutes with a periodic check of temperature every five minutes.

Figure 5.18 Plot showing the temperature dependence of magnetic-field assisted MacEtch with and without an external magnetic field. Error bars showing standard deviation in measurement of etch depths from 25 data points.
With the presence of external magnetic field of 0.22 T, the etch rate is enhanced as shown in the plot given in Figure 5.18. We etched the samples under several different temperatures ranging from 20-50 °C and compared the etch rate with (shown in red and blue) and without (shown in black) magnetic fields. The etch rates increasing with the bath temperature indicate a reduction in the energy barrier required for the oxidation or dissolution steps in the MacEtch process. Under the current study, we can only describe the activation energy for silicon pillar formation using MacEtch, and not isolate the energy required for the individual oxidation or dissolution steps.

Figure 5.19 Arrhenius plot for rate of formation of MacEtch-produced micropillars with and without an external magnetic field. Error bars showing standard deviation in measurement of etch depths from 25 data points.

From the corresponding Arrhenius plot as shown in Figure 5.19, we can notice that the slope of the plot corresponding to the samples etched under magnetic field has a lower slope which corresponds to a lower activation energy. This indicates that the presence of magnetic field impacts
the falling or sinking rate of the catalyst film during the course of MacEtch which could probably push the catalyst film to come in close proximity to the silicon atoms underneath, and increasing the mass transport of by-products formed during the course of MacEtch. The rate of formation of micropillars (k expressed in nm/s) is given by,

\[ k = A \exp(-E_a/RT) \] (5.1)

where \( E_a \) is the activation energy of formation rate (J/mol/K), \( A \) is the rate-coefficient extracted from the intercept, \( R \) is the gas constant (8.314 J/mol/K) and \( T \) is the temperature. By writing the Equation 5.1 in natural-logarithmic form, we have

\[ \ln k = \ln A - E_a/RT \] (5.2)

<table>
<thead>
<tr>
<th>Case</th>
<th>Slope</th>
<th>Y-Intercept</th>
<th>( E_a ) (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B=0 T</td>
<td>-1.77</td>
<td>0.19</td>
<td>14.74</td>
</tr>
<tr>
<td>B=0.22 T</td>
<td>-1.43</td>
<td>0.17</td>
<td>11.93</td>
</tr>
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<td>B=0.3 T</td>
<td>-1.38</td>
<td>0.06</td>
<td>11.45</td>
</tr>
</tbody>
</table>

Table 5.1 Summary of values extracted from the Arrhenius plot shown in Figure 5.19.

From the slope and Y-intercept obtained from the Arrhenius plot given in Figure 5.19, we have summarized the values in Table 5.1. As seen from the summary, the activation energy of formation of micropillars is reduced by \(~19\%) with the application of external magnetic field of 0.22 T. Also, with a field of 0.3 T, the activation energy is further reduced to \(~22\%) of that without an external field. With this trend, it would be an educated guess to expect the activation energy to be further reduced with an application of a field of more than 0.3 T. But this can be verified by performing more follow-up experiments in the future.
5.6 Influence of Magnetic Pulling Force on MacEtch

In all our previous reports on magnetic-field assisted MacEtch, we have used an external magnetic field to pull the isolated catalyst disks in a vertical direction, and also to enhance the etch rate. It would be helpful to improve the current level of understanding of this magnetic field-enhanced MacEtch if we could develop a physical model to illustrate the mechanics of this process. With this objective in mind, we have performed a set of experiments using permanent magnets that can generate an external magnetic field required for this study. We will briefly describe the specification of the magnets used for this study, and then measure the magnetic pull force generated by the current configuration of the permanent magnets.

The following kinds of permanent magnets that are cylindrically magnetized were used for all of our experiments. It should be noted that the estimation of magnetic pull force is available only for these cylindrically magnetized permanent magnets relating this force with the residual flux density in Gauss.

1. NdFeB Disc Magnet 2” diameter * 1/4” thick, N42 grade, $B_r = 13200$ Gauss [52]
2. NdFeB Block Magnet 2” * 2” * 1/4”, N48 grade, $B_r = 14200$ Gauss [53]
3. NdFeB Block Magnet 2” * 2” * 1”, N52 grade, $B_r = 14800$ Gauss [54]

The vendors selling permanent magnets have provided online resources to calculate the magnetic pull force of permanent magnets on their websites [55]. The following relationship is used for estimating the pull force of bar magnets that considers the geometry of the magnets which fits well with the specification of the magnets tested by the vendor.
Permanent magnets used for h-MacEtch experiments. (Left) N42, (Middle) N48, and (Right) N52.

\[ F_z = 0.576B_r^2tA^{0.5} \]  \hspace{1cm} (5.3)

where \( F_z \) is the magnetic pull force of a bar magnet (lbs.), \( B_r \) is the flux density (kGauss), \( t \) is the thickness of magnetic surface (inches), and \( A \) is the surface area (square inches).

To gain a better understanding of the physics behind the relationship, the readers are referred to the analysis of the magnetic pull force arising between the poles of an electromagnet [56]. For an electromagnet characterized by the area \( A \), the magnetic flux density \( B \), and the relative magnetic permeability \( \mu_r \), the magnetic pull force is given by,

\[ F = A \frac{B^2}{2\mu_0\mu_r} \]  \hspace{1cm} (5.4)

where \( \mu_0 \) and \( \mu_r \) are the magnetic permeability of free space and relative permeability of the medium, respectively. We varied the magnetic field intensity by adjusting the number of permanent magnets stacked together. Using two N42 and three N48 permanent magnets, we
achieved a B-field of 0.22 T and 0.3 T (measured using a Gauss meter from F. W. Bell) respectively. Using the relationship given in Equation 5.3 and the specification of the permanent magnets, we can calculate the magnetic pull force for the configurations used in our study. The values are shown below in Table 5.2.

Table 5.2 Summary of the estimation of magnetic pull force used for our study.

<table>
<thead>
<tr>
<th>B (T)</th>
<th>A (square inches)</th>
<th>t (inches)</th>
<th>Magnetic pull force $F_z$ (lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.22</td>
<td>3.14</td>
<td>1</td>
<td>494</td>
</tr>
<tr>
<td>0.3</td>
<td>4</td>
<td>1.5</td>
<td>1555</td>
</tr>
<tr>
<td>0.45</td>
<td>4</td>
<td>1</td>
<td>2333</td>
</tr>
</tbody>
</table>

In all our experiments, we used a MacEtch solution of 20 ml of HF, 5 ml of H$_2$O$_2$, 16 ml of DI, and 16 ml of IPA heated to 40 °C for 10 minutes. The samples were rinsed with DI and blown dry with a Nitrogen gun. After drying, the samples were imaged using Hitachi S-4800 Scanning Electron Microscopy (SEM), and the heights of the pillars etched were measured from the tilted-view SEM images. We measured the average and standard deviation of etch depths of 25 micropillars for all the cases studied here. The corresponding values are shown as symbols and error bars in the figures described herein.

In addition, we also performed a COMSOL simulation of spatial distribution of magnetic flux density around the pole of the N52 permanent magnet with a width of 2 inches and thickness of 1 inch used in our study. As shown in the 2D contour plot of magnetic flux density in Figure 5.21, the magnitude of the flux density starts decreasing as you move away from the edge of the
magnet. Also, the flux density near the surface of the magnet is roughly 4500 Gauss as shown by the red colored region, and this matches very closely with the experimentally measured value of magnetic flux density near the surface of the permanent magnet. We can also notice that the magnetic flux density at a distance of about an inch from the surface degrades to almost half of the value near the top surface.

Figure 5.21 COMSOL simulation showing 2D spatial distribution of residual magnetic flux density around the N52 permanent magnet used in our study (Courtesy: Ivan A. Shchelkanov).

5.6.1 Reversal of Polarity of Permanent Magnet

In order to understand the impact of the direction and magnitude of the magnetic pull force, we performed two different sets of experiments. In the first case, we varied the magnitude of the magnetic field intensity by using different types of magnets shown in Figure 5.20, and compared
the etch depth with the case of zero magnetic field. In addition, we also flipped the polarity of the permanent magnet as shown in the schematic diagram in Figure 5.22 to understand the impact of the direction of the magnetic lines of force. From this experiment, we can verify whether reversing the direction of the magnetic field would impact the direction of the external pull force acting on the ferromagnetic material. In the second case, we reversed the direction of the attractive magnetic force by moving the permanent magnet to the other side of the Si chip such that the direction of motion of catalyst is opposite to the direction of magnetic pull force.

Figure 5.22 (a) Schematic diagram illustrating the experimental setup used to perform MacEtch under different polarities of permanent magnet and (b) photographic images of magnetic field measurements using a Gaussmeter with the probe tip placed near the North and South poles of a N52 permanent magnet.

In Figure 5.23, we have summarized the etch depths obtained from mesh patterns of different dimensions with and without magnetic fields after 10 minutes by placing the Teflon
beaker facing both the North and South poles of the permanent magnet. As seen in the plot, the etch rate is considerably enhanced with the application of an external magnetic field facing both the North and South poles. This is attributed to the enhanced magnetic pull force of attraction acting on the ferromagnetic layer that is sandwiched between the top and bottom gold layers. This trend is consistent with the different designs (D1-D4) used in this study. When compared to the samples etched without an external magnetic field ($B = 0$), the ones etched with an attractive magnetic force are sinking to the bottom at a higher rate as the permanent magnet placed underneath the silicon chip tries to pull the 10 nm thick Fe layer toward it in addition to the force due to gravity and vdW forces acting on the metal film. Clearly, this field reversal experiment demonstrates that the impact due to the external magnetic field arises only from the pull-down force acting on the Fe layer which does not depend on the polarity of the external magnetic field.

![Figure 5.23 Variation of MacEtch rate with the magnitude of external magnetic pull force. Error bars showing standard deviation in measurement of etch depths from 25 data points.](image-url)
Another interesting observation from the plot in Figure 5.23 is the saturation of the etch depth for the cases of D1 and D2 having a smaller feature size. Since there is a difference in surface area of the ferromagnetic film for the four cases studied here, we hypothesize the “areal effect” based on the pressure applied by the external magnetic pull force on the metal film (refer to Appendix D for the calculation of magnetic pressure). For the cases D1 and D2 showing saturation in etch depth, the relatively larger area of catalyst film is limiting the further increase in the pressure applied on the catalyst film during etching, and thus, the magnetic field is not strong enough to push the film down. But in the cases of D3 and D4, with a relatively smaller surface area, the force applied is sufficient to linearly increase the pressure applied on the film within the regime of the external magnetic field considered here. However, with further increase in the magnitude of the external magnetic field, we should anticipate a saturation in the etch depth even for the cases D3 and D4, as the magnetic pull force can only work to some maximum for a given surface area of the catalyst film beyond which the external pressure cannot be further increased. This observation also reveals that the rate-limiting step in the MacEtch process for these large feature sizes is the anodic reaction of oxidation of Si (which varies with the surface areal density of Si atoms) under the metal-silicon interface which is strongly impacted by the presence of the external pressure produced by the attractive magnetic pull force directed toward the bottom of the surface. The same trend on the rate-limiting step for large feature sizes can also be correlated with the formation rate of Si micropillars of different feature sizes (800 nm, 550 nm and 200 nm) made using soft lithography as reported in Figure 3.2 in Section 3.3. It should be noted that the oxidation rate of Si underneath the metal mesh layer used for this study is the rate-limiting step which is directly related to the diffusion time of the volatile by-products that gets formed during the anodic
reaction, and the quantity of acid and oxidant available for each of the feature sizes (which was kept as a constant for all the cases).

In addition, by looking at the linear trend in the variation of etch depth with the magnetic pull force corresponding to D4, we can hypothesize that by projecting this trend to an etch depth of zero, a very high magnetic pull force of ~4000 lbs applied in an opposing direction should be sufficient to resist the MacEtch process from happening, and hence, we can consider this phenomenon for applications where adjustment is needed for the etch rate of multiple layers of materials undergoing etching in a sequential order to a given value without adjusting the concentration of etchants. This also motivates us to explore the concept of magnetic-field resisted MacEtch. For etching stacks of semiconducting materials (e.g. a heterojunction-based device), we can consider using an external magnetic field as an external control variable to achieve a uniform etch rate for different layers.

As seen from Figure 5.24, the etch depth at zero magnetic field shows a square root dependence on the width (D) (or feature size) of the pillars. This can be understood based on the square root dependence of diffusivity of reactants in the MacEtch solution and the end products that are formed during the course of etching. It should be noted that the etch rate for these large feature sizes should depend both on the diffusion time of the end products and the availability of reactants and products that get formed. Since the diffusion time of the end products has a dependence of the inverse of the square root of width (D^{-0.5}), and the availability of the reactants can be related to the size of the outer periphery of the pillars (4*D in case of our square-shaped pillars), we could expect a square root dependence on the feature size (D^{0.5}). This matches with the trend measured in the experimental observation for the case of zero magnetic field as shown in Figure 5.24.
Figure 5.24 Variation of MacEtch rate of silicon micropillars of different feature sizes in the absence of an external magnetic field. Error bars showing standard deviation in measurement of etch depths from 25 data points.

5.6.2 Reversal of Direction of Magnetic Force of Attraction

Figure 5.25 Plots showing (left) variation of magnetic pull force in free space, and (right) etch depth obtained from design D4 after 10 minutes as a function of distance of separation.
In the experiments described in Section 5.6.1, we have kept the direction of magnetic force of attraction always pointing from top to bottom, and hence, the negative magnitude of residual magnetic flux also resulted in a symmetric trend in the etch depth of the pillars formed. As shown in Figure 5.25, the magnetic pull force calculated from the measured flux density in free space at different distances of separation from either poles of the permanent magnet has a symmetric shape, and the force starts decaying in an inverse-square fashion as we move away from the poles.

Figure 5.26 Schematic representation and photographic images of the experimental setup used for reversing the direction of the magnetic force of attraction on the catalyst during MacEtch.

In order to make use of the external magnetic pull force in an opposing direction, we modified the position of the permanent magnet with respect to the Teflon beaker. As shown in
Figure 5.26, the permanent magnet was moved to the top of the Teflon beaker, and carefully held at different heights above the MacEtch solution. In this way, we can attract the ferromagnetic layer toward the top with the magnetic pull force, and understand its impact on the MacEtch rate. Proper nitrile gloves should be worn while holding the permanent magnet inside the Teflon beaker as a safety precaution working with the HF vapors coming from the etch solution.

![Graph showing impact of magnetic pull force on MacEtch depth](image)

**Figure 5.27** Impact of reversal of direction of magnetic pull force of attraction on MacEtch. Error bars showing standard deviation in measurement of etch depths from 25 data points.

We performed a series of experiments with a piece of N52 permanent magnet placed near and far away from the Si chip both above and below the Teflon beaker. It should be noted that the
magnetic field measured for calculating the pull force in Figure 5.25 corresponds to the field intensity in free space as the probe tip of the Gaussmeter was in open air directly above the magnet. However, in our current experimental setup, for the case where the magnet is placed above the beaker, the magnetic field lines have to pass through both air and an ionic liquid medium before reaching the Fe layer immersed inside the MacEtch solution. This can cause degradation in the magnitude of the magnetic pull force of attraction due to the change in media surrounding the source of the magnetic field.

In Figure 5.27, we have summarized our measurement of etch depths from all four different dimensions of pillars studied in this section, with the magnet kept at several different distances of separation from the Si chip undergoing MacEtch. In regions A and D, where we have moved sufficiently away from the influence of the external magnetic field, the etch depth obtained matches very closely to the value obtained without an external magnetic field reported in Figure 5.23. Also, this correlates with the drastic reduction of the magnetic pull force beyond a distance of separation of ~1 inch as shown in Figure 5.25. In region C, we notice an inverse square relationship in the reduction of etch depth with a distance which matches with the trend for the magnetic pull force while moving away from the pole of the permanent magnet. This indicates that the magnetic pull force of attraction combines additively with the other forces, and thus, the film sinks faster with the increase in the pressure applied by the external field. It should also be noted that the same argument using the pressure applied by the magnetic pull force used to explain the areal effect can be used here to hypothesize the trend in the values of etch depths measured for different dimensions (D1-D4) of the pillars etched.

Interestingly, in region B, we have observed a reduction in the etch depth of pillars when compared to region A. This implies that the magnetic pull force of attraction acting in the upward
direction in this case is trying to reduce the physical contact between the metal film that is sinking due to force of gravity, and the silicon underneath. However, the trend in etch depth is not symmetric with respect to region C even though the distance of separation is the same. This absence of an inverse square relationship with a distance of separation in region B can be viewed in terms of the different nature of distribution of magnetic field lines around the ferromagnetic layer immersed inside the MacEtch solution due to the presence of two different media-air and ionic liquid, unlike the case in region C where there is no such influence.

To test our hypothesis on the difference in medium through which the magnetic lines of field are passing, we have performed a measurement of magnetic field intensity of the N52 permanent magnet through an ionic liquid and air medium as shown in Figure 5.28. As seen from the photographic images, the magnetic field intensity shows a drop of 53 Gauss after passing through the ionic liquid medium, and this results in a lowering of magnetic pull force by 4.5 lbs.

Figure 5.28 Photographic images of measurements of magnetic field intensities of an N52 permanent magnet using a Gaussmeter measured after passing through an (left) ionic liquid medium and (right) an air medium.
found by calculating using Equation 5.3. We can conclude that the asymmetric trend in etch rate in region B is due to the nature of the distribution of the magnetic lines of forces in an ionic liquid medium. In order to bring this trend symmetric to that found in region C, we should consider applying a higher magnetic field that can suppress the drop in magnetic pull force due to the presence of the ionic liquid medium. Also, we can notice a difference in the level of reduction of the etch depth for the four different dimensions (D1-D4) which can also be explained based on the difference in magnetic pressure as done before.

Figure 5.29 (a) Schematic representation of the MacEtch process showing the mass transport of etchants and end products. Physical model of forces acting on the catalyst film with (b) an upward and (c) a downward magnetic force of attraction.

Further, to illustrate the difference in etch trends for the cases shown in regions B and C, we have developed a physical model as shown in Figure 5.29, to illustrate the difference in pressure
applied on the ferromagnetic layer under different directions of external magnetic force of attraction. Let us denote the mass of the catalyst film sinking down as $m$ and hence the force due to gravity would be $mg$ acting downward. In addition, we should consider the predominant forces due to vdW forces and other bonding forces which are collectively represented as $F_{\text{chemical}}$ in our model. Let $F_1(x)$ and $F_2(x)$ denote the magnetic force of attraction acting in the upward and downward directions respectively, where $x$ is the distance of separation between the Teflon beaker and the permanent magnet. Since MacEtch relies on oxidizing the Si atoms underneath the catalyst film, and dissolution of the oxidized Si atom, we are defining a mathematical function ($Z(F(x))$) that defines the small distance of separation between the metal and Si during the course of etching. Under the absence of an external magnetic field, let us assume that there is a minimum value for this function and denote it as $Z_0$.

From the physical model in Figure 5.29, we can notice that there are two terms involved in the function describing this distance of separation: a field-dependent term and a field-independent term.

$$Z = Z_0 + Z(F_1(x)) \quad \text{(5.5)}$$

$$Z = Z_0 - Z(F_2(x)) \quad \text{(5.6)}$$

Equations 5.5 and 5.6 correspond to regions B and C, respectively. If the external magnetic force opposes the force due to gravity, the distance of separation (or $Z(F(x))$) increases and vice versa. For regions A and D, the value of this gap function would be approximately equal to $Z_0$ due to the lack of influence of an external magnetic field. This physical interpretation can help us to understand the enhancement or retardation of the speed of motion of the catalyst with an embedded ferromagnetic material used for MacEtch. In the future, it would be interesting to extend this theory.
to the multi-directional motion of catalyst by making suitable modifications to the direction of application of the external magnetic field in three-dimensional space.

As shown in Figure 5.30, we have performed a comparison of the magnetic pull force measured in air (black curve) and ionic liquid medium (blue curve), and the magnetic pull force obtained from the magnitude of magnetic flux density from the COMSOL simulation (red curve) shown in Figure 5.24. It should be noted that the magnetic flux density measured in air medium is only slightly larger than the corresponding value measured in ionic liquid medium for large distances of separation between the magnetic pole and the silicon chip. As we move the magnet closer to the surface of the ionic liquid, we can see a significant decrease in the magnitude of the

![Graph showing the variation of magnetic pull force with distance of separation in different media.](image)

**Figure 5.30** Variation of measured and simulated values of magnetic pull force in different media as a function of distance of separation.
flux density due to the interaction between the contents of the ionic liquid with the magnetic lines of force. Hence, the magnetic pull force is not sufficient to increase the gap between the metal film and silicon substrate (as in case (b) in Figure 5.28), and now, Equation 5.5 will hold true. This can also be understood from the square dependence of magnetic pull force on the flux density of the permanent magnet. For smaller flux densities at larger values of x, both $F_1(x)$ and $F_2(x)$ are comparable in magnitude but opposite in direction. But for larger flux densities, clearly, $F_2(x)$ will be less than $F_1(x)$, and this matches with the spread in values between the force measured in the ionic liquid medium (shown in blue) and the force measured in the air medium (shown in red) in Figure 5.30. The schematic diagram shows the difference in spatial arrangement of the magnet and Teflon beaker for the two cases described here. Now, using the differences in the magnitude of the magnetic pull force measured in the air and ionic liquid media, we can justify the lack of symmetry in the variation of etch depth with distance of separation in region B of Figure 5.27. Also, the black and red curves corresponding to D1 and D2, respectively showing a relatively lower dip in the etch depth when compared to the corresponding values in region A can be explained by this difference in the magnitude of magnetic pull force that tries to widen the gap in between the metal film and Si underneath to different levels.
CHAPTER 6

CONCLUSIONS

In this dissertation, we have briefly reviewed the history of the MacEtch process. Then, we described the research related to the study of porosity control in degenerately doped silicon nanowires. We also demonstrated the tunable aspect ratio of silicon nanowire fabrication, and also demonstrated the need for low-temperature MacEtch to reduce porosity during fabrication. Next, we summarized our work on performing MacEtch in Gallium Arsenide where we first started with a single layer of GaAs as the starting material and then demonstrated the applicability of this technique to etch a homojunction formed in GaAs into pillars in order to demonstrate LED applications. We also explored the parameter space in the concentration of etchants for different kinds of doping levels and types. After this, we described the use of MacEtch in Silicon-on-Insulator substrates to etch periodic holes of sub-micron feature sizes in order to extend this technique to passive photonic device applications. Here, we also emphasized the need for an external magnetic field to etch vertical holes of desired aspect ratios, and also measured the performance of a PhC-MR made using this approach. At the end, we reviewed our latest findings on multi-directional MacEtch using an external magnetic field generated by a stack of permanent magnets and a unique configuration called “Halbach array” to generate a uniform field along the plane. We also performed some quantitative studies on the enhancement of the MacEtch rate under the application of different ranges of magnetic fields and developed a model that can be used for empirically determine the expected etch rate. Also, we explored metal back-filling using silver on the holes etched using MacEtch to perform a feasibility study on using this approach to demonstrate tunable metamaterials.
CHAPTER 7

FUTURE DIRECTIONS

7.1 Design and Testing of Programmable $h$-MacEtch Apparatus

One of the major challenges with meeting the objectives of this dissertation was the development of an apparatus for achieving different magnitudes of magnetic field intensities along different directions in a programmable way. We explored design options using both permanent magnets and electromagnets. In this section, we will briefly describe our efforts with the two different designs and also suggest ways to improve the limitations in our current design.

7.1.1 Stacking of Halbach Arrays

Our current results with the X directional drifting of the catalyst during $h$-MacEtch motivated us to extend this concept to a programmable apparatus. In Figure 7.1, we have shown a schematic model of the design that uses a stack of circular Halbach arrays. The design involves precise positioning of Halbach arrays with the same inner diameter at a distance of separation that is sufficient to avoid the influence of the neighboring array. In addition, the circular Halbach arrays are positioned in the stack with different orientations depending upon the intended polarity of the magnetic field at the specific height from the bottom. Also, we propose to have a vertical stack of permanent magnets at the bottom to provide the Z directional magnetic field. The magnitude of this Z directional field can be altered by simply replacing the stack to get the desired magnitude of field. As an alternate option, we can also consider rotating the cylindrical rod inserted inside the center core to change the polarity of the magnetic field. The rod can be raised or lowered with the help of a linear servo motor having a relatively large travel distance (in few tens of microns), and the exact position of the rod can be entered using a PC with a LabVIEW interface that can pass on the input signal to the servo motor. Using this strategy, the user has an option to enter the sequence
of etch steps that are required for altering the magnitude and polarity of the field inside the air core.

Figure 7.1 Schematic representation of the programmable MacEtch apparatus using a stack of circular Halbach array and a servo motor.

Even though this design appears to be simple and easy to create, the major limitation with the current state-of-the-art in the design of a circular Halbach array is the restriction on the inner diameter. Vendors supplying such circular Halbach arrays are unable to increase this inner diameter to any size more than an inch due to the inability to maintain a uniform field strength in the air core for larger diameters. This restricts this design for application only for smaller Si chips.
that are used for test purposes in academic research purposes. In order to scale this design to 2 or 4 inch wafers, we must explore alternate approaches to design the circular Halbach array, for example, by nesting multiple Halbach arrays to increase the concentration of the field.

### 7.1.2 3D Programmable Electromagnets

![Scheme for implementing 3D programmable magnetic field using electromagnets.](image)

**Figure 7.2 Scheme for implementing 3D programmable magnetic field using electromagnets.**

In order to achieve a programmable magnetic field, we also considered the use of electromagnets. In this approach, as shown in Figure 7.2, we use a High-Temperature Superconducting (HTS) coil in three dimensions and a bipolar power supply that can alternate the polarity of the magnetic field. The power supplies are connected to a control unit that receives signal from a PC with LabVIEW interface. The sample undergoing etching is placed in the middle of the HTS coils as shown in Figure 7.2. The main limitations with this approach are the cost of
the electromagnets made using the HTS coils and the bore size of the electromagnets is only a few millimeters which restricts the size of the sample that can be etched. As this approach is cost-prohibitive, we decided not to implement this idea into a prototype. However, if the vendors manufacturing the electromagnets can reduce the cost of the magnets and also increase the volume of the inner core, this approach may be extended to large wafers in the future.

7.2 Metal Electro-Filling for Tunable Metamaterials

Toward our future goal of demonstrating tunable metamaterials, we performed electrofilling of holes etched using MacEtch with silver. In our first set of experiments, we used an array of circular disks of catalyst metal with a diameter of ~300 nm and pitch of ~5 µm, and etched the samples to achieve an etch depth of ~260 nm. These samples were subjected to electrodeposition of silver to fill the holes with the metal. The SEM images in Figure 7.3 show the metal overflowing from the holes after the electrodeposition process. We are currently working on repeating the electrofilled process in high aspect ratio structures as our end goal in this dissertation is to demonstrate metallic nanostructures with controlled chirality having a non-linear structure with very high aspect ratios.

Figure 7.3 (a-c) Top-view SEM images of MacEtched samples electrofilled with silver under different magnifications.
APPENDIX A

SUMMARY OF DOPING CONDITIONS USED FOR POST-DOPING OF SILICON NANOWIRE ARRAYS

Table A.1 Summary of doping conditions used for p-type and n-type silicon nanowire arrays with different sidewall roughness.

<table>
<thead>
<tr>
<th>Type</th>
<th>Sidewall roughness in nm (roughening process time shown inside parentheses)</th>
<th>Drive-in conditions</th>
<th>Diameter (nm)</th>
<th>2PP Measured resistivity (milliOhm-cm)</th>
<th>Calculated resistivity without contact contribution (milliOhm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P+</td>
<td>0 nm (smooth)</td>
<td>950 °C, 5 min</td>
<td>82-191</td>
<td>5-13</td>
<td>0.63-1.80</td>
</tr>
<tr>
<td></td>
<td>0 nm (smooth)</td>
<td>950 °C, 10 min</td>
<td>84-113</td>
<td>8-16</td>
<td>0.22-0.66</td>
</tr>
<tr>
<td></td>
<td>2 nm (14 sec)</td>
<td>950 °C, 10 min</td>
<td>86-107</td>
<td>43-55</td>
<td>1.37-1.57</td>
</tr>
<tr>
<td></td>
<td>2.25 nm (17 sec)</td>
<td>950 °C, 10 min</td>
<td>68-150</td>
<td>48-80</td>
<td>1.11-4.27</td>
</tr>
<tr>
<td>N+</td>
<td>0 nm (smooth)</td>
<td>900 °C, 10 min</td>
<td>84-128</td>
<td>30-69</td>
<td>0.74-1.63</td>
</tr>
<tr>
<td></td>
<td>0 nm (smooth)</td>
<td>950 °C, 10 min</td>
<td>47-130</td>
<td>2-23</td>
<td>0.21-1.09</td>
</tr>
</tbody>
</table>
In MacEtch, the metal catalyst acts as the cathode and the semiconductor acts as the anode. Table B.1 lists relevant half reactions involving chemical species used for etching in this dissertation, as well as possible products and participating reactants in the overall reaction.

**Table B.1 Half-cell electrochemical potentials.**

<table>
<thead>
<tr>
<th>Cathode Reaction (metal)</th>
<th>$E^0$/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO$_4^-$ + 8H$^+$ + 5e$^-$ $\rightarrow$ Mn$^{2+}$ + 4H$_2$O</td>
<td>1.507</td>
</tr>
<tr>
<td>MnO$_4^-$ + 4H$^+$ + 3e$^-$ $\rightarrow$ MnO$_2$ + 2H$_2$O</td>
<td>1.679</td>
</tr>
<tr>
<td>H$_2$O$_2$ + 2H$^+$ + 2e$^-$ $\rightarrow$ 2H$_2$O</td>
<td>1.776</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anode Reaction</th>
<th>$E^0$/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga $\rightarrow$ Ga$^{3+}$ + 3e$^-$</td>
<td>0.549</td>
</tr>
<tr>
<td>2As + 3H$_2$O $\rightarrow$ As$_2$O$_3$ + 6H$^+$ + 6e$^-$</td>
<td>-0.234</td>
</tr>
<tr>
<td>As + 2H$_2$O $\rightarrow$ HAsO$_2$ + 3H$^+$ + 3e$^-$</td>
<td>-0.248</td>
</tr>
<tr>
<td>HAsO$_2$ + 2H$_2$O $\rightarrow$ H$_3$AsO$_4$ + 2H$^+$ + 2e$^-$</td>
<td>-0.560</td>
</tr>
</tbody>
</table>

**Overall Reaction**

GaAs + MnO$_4^-$ + H$^+$ $\rightarrow$ Ga$^{3+}$ + As$^{3+}$ + Mn$^{2+}$ + H$_2$O

**Overall reaction with possible forms of the products (balanced)**

GaAs + 2KMnO$_4$ + H$_2$O + 5HF $\rightarrow$ HAsO$_2$ + GaF$_3$•3H$_2$O + 2MnO$_2$ + 2KF

3GaAs + 8KMnO$_4$ + 17HF + 5H$_2$O $\rightarrow$ 3H$_3$AsO$_4$ + 3(GaF$_3$•3H$_2$O) + 8MnO$_2$ + 8KF

10GaAs + 12KMnO$_4$ + 33H$_2$SO$_4$ $\rightarrow$ 10HAsO$_2$ + 12MnSO$_4$ + 6K$_2$SO$_4$ + 5Ga$_2$(SO$_4$)$_3$ + 28H$_2$O

10GaAs + 16KMnO$_4$ + 39H$_2$SO$_4$ $\rightarrow$ 10H$_3$AsO$_4$ + 16MnSO$_4$ + K$_2$SO$_4$ + 5Ga$_2$(SO$_4$)$_3$ + 24H$_2$O
APPENDIX C

THEORETICAL CALCULATION OF SIZE OF HYDROGEN GAS BUBBLES RELEASED DURING MACETCH

We have performed a theoretical calculation of the size of the Hydrogen gas bubbles that are released during the etch process and compared the number to the diameter of the gold catalyst. From the MacEtch mechanism discussed in Section 2.2, let us consider the chemical reactions involved in the process once again.

At Cathode: \( \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + 2\text{h}^+ \)  
(Local reduction)

\( 2\text{H}^+ \rightarrow \text{H}_2 + 2\text{h}^+ \)  
(Hydrogen gas formation)

At Anode: \( \text{Si} + 6\text{HF} + 4\text{h}^+ \rightarrow \text{H}_2\text{SiF}_6 + 4\text{H}^+ \)  
(Dissolution of silicon)

Net reaction: \( \text{Si} + 6\text{HF} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} + \text{H}_2 \)

As we can see from the chemical equations above, for every one mole of Si atoms reacting with one mole of Hydrogen peroxide, one mole of Hydrogen gas gets liberated. In the case under study, we used an array of dot patterns with a diameter of 125 nm and pitch of 200 nm. Also, there were 1800 rows and 250 columns of dots in our layout for e-beam writing. Since the surface areal density of Si atoms for a (100) Si wafer is \( 6.78 \times 10^{14} \, \text{cm}^{-2} \), the number of Si atoms that are under the Au catalyst disk, denoted by \( A \), is given by,

\[
A = 6.78 \times 10^{14} \times 1800 \times 250 \times 3.14 \times (125 \times 10^{-7})^2 / 4
A = 3.74 \times 10^9 \, \text{Si atoms}
\]

Therefore, the number of moles of Si undergoing oxidation, denoted as \( N \), is given by,

\[
N = 3.74 \times 10^9 / (6.023 \times 10^{23}) = 6.21 \times 10^{-14}
\]

By looking at the net reaction of MacEtch process, we can state that for every \( N \) moles of Si atoms, we must liberate \( N \) moles of Hydrogen gas bubbles. But this is only possible when we have at least \( N \) moles of Hydrogen peroxide reducing into water at the cathode. In our case, we are
limiting the number of Si atoms undergoing oxidation to a small percentage, denoted as \( Y \), and is given by,

\[
Y = (9.79 \times 10^{-6} \times x \times N)
\]

where \( x \) is the volume in microliters of 30\% Hydrogen peroxide used for the trial. Knowing the number of Si atoms that can be oxidized during MacEtch, we can estimate the volume of Hydrogen gas bubbles that can be generated during the etch process from the available amount of Si atoms using the ideal gas equation \((PV = nRT)\) where the pressure \((P)\) is 1 atm and temperature \((T)\) is 300 K.

**Table C.1 Summary of dimension of gas bubbles liberated under different etch conditions.**

<table>
<thead>
<tr>
<th>Volume of H(_2)O(_2) (x in (\mu)L)</th>
<th>Number of moles of Si atoms oxidized ((Y))</th>
<th>Total volume of Hydrogen gas generated (in (\mu)L)</th>
<th>Radius of gas bubble (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.08*10(^{-19})</td>
<td>1.5*10(^{-11})</td>
<td>153</td>
</tr>
<tr>
<td>5</td>
<td>3.04*10(^{-18})</td>
<td>7.5*10(^{-11})</td>
<td>262</td>
</tr>
<tr>
<td>20</td>
<td>1.21*10(^{-17})</td>
<td>3*10(^{-10})</td>
<td>415</td>
</tr>
</tbody>
</table>

In Table C.1, we have listed the values of the volume of Hydrogen gas bubble that could be generated, and the corresponding radius of the bubble for the three different cases studied in our experiments. It should be noted that, for the case with 1 \(\mu\)L of H\(_2\)O\(_2\), the radius of the gas bubble is smaller than the pitch (200 nm) used in our study. This is the only case where we see a stable sinking of the catalyst disk during the MacEtch process. As a future work, it would be worth exploring MacEtch at higher pressures to verify our hypothesis on the lack of catalyst stability during MacEtch using the volume of gas bubbles liberated.
APPENDIX D

CALCULATION OF MAGNETIC PRESSURE APPLIED ON IRON FILM

For all the mesh patterns considered in our experiments, we use a length and width of 2 mm each. Knowing the width and pitch of the square-shaped openings in the mesh pattern, we can calculate the total surface area of the iron film used in our study. Table D.1 summarizes the magnetic pressure (in lbs/mm²) applied on the iron film at different values of magnetic pull forces.

Table D.1 Summary of magnetic pressure applied on iron film.

<table>
<thead>
<tr>
<th>Design</th>
<th>D (µm)</th>
<th>P (µm)</th>
<th>Area of Fe² (mm²)</th>
<th>( P_m ) (( F_z = 494 ) lbs)</th>
<th>( P_m ) (( F_z = 1555 ) lbs)</th>
<th>( P_m ) (( F_z = 2333 ) lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>10</td>
<td>30</td>
<td>3.742</td>
<td>132.015</td>
<td>415.553</td>
<td>623.463</td>
</tr>
<tr>
<td>D2</td>
<td>20</td>
<td>60</td>
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<tr>
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<td>133.1178</td>
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<td>628.671</td>
</tr>
</tbody>
</table>
APPENDIX E

RECIPE FOR DRYING OF HIGH ASPECT RATIO SILICON NANOPILLARS

In order to dry the samples with high aspect ratio silicon nanopillars made using MacEtch, we recommend not to rinse the samples in deionized water due to its relatively high surface tension causing cluttering of pillars. Instead, we recommend the following sequence of rinsing steps: (1) 15-20 seconds in methanol, (2) 15-20 seconds in IPA, and (3) drying the sample on a hot plate kept at above 100 °C. In addition, the use of a Nitrogen gun for blow drying should also be avoided to minimize the cluttering of pillars during our processing.
REFERENCES


Metal-assisted electrochemical etching of silicon,” *Nanotechnology*, vol. 21, no. 46, p. 465301, Nov. 2010.


[54] https://www.kjmagnetics.com/proddetail.asp?prod=BY0Y0X0-N52.
