2011

Electrochemical etching of isolated structures in p-type silicon

Joel Nino Bugayong
Louisiana State University and Agricultural and Mechanical College, joel14thwarrior@yahoo.com

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses
Part of the Chemical Engineering Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_theses/4084

This Thesis is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Master’s Theses by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
ELECTROCHEMICAL ETCHING OF ISOLATED STRUCTURES
IN P-TYPE SILICON

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
In partial fulfillment of the
Requirements for the degree of
Master of Science in Chemical Engineering

In

The Department of Chemical Engineering

By
Joel Niño G Bugayong
B.S., University of the Philippines at Los Baños, 2004
May 2011
ACKNOWLEDGMENTS

I would like to thank the following people for their valuable contributions to the success of my thesis.

- Prof John C Flake, research advisor
- Jeff Desroches, Dr. Peter Wrschka, and ATMI
- Dr. Yoonyoung Jin, CAMD-RIE
- Dr. Greg Book, LPCVD, MiRC-GaTech
- Dr. Congmei Cao, SEM; Dr. Ying Xiao, Bio SEM and Sputter
- Dr. Gregory Griffin, Dr. Francisco Hung, Dr. James Henry – committee members
- Research colleagues: Purnima, Minnie, Wanli, Sai, Dr. Maoming Ren, Dr. John Peter Ngunjiri, John F., John T., Kang, Goucheng, Fareed, Shaloma.
- Susanna Dixon, thesis editor

I would also like to thank the following research centers for providing the tools and equipment to complete my research work.

- Center for Advance Microstructures and Devices, LSU
- Materials Characterization Center, LSU
- Socolofsky Microscopy Center, LSU
- Microelectronics Research Center-GaTech

Thanks to...

- My Lord and Savior, Jesus Christ
- My parents, my siblings and their family, my girlfriend Patrisha J. Pham, and Tita
- My hyper brothers from Victory Christian Fellowship: Kuya Pepeng, Paeng, Isko and family, Jowell B1
- My fellow Filipino students at LSU
- My American host family, Tanner and Stephanie Martinez and their 4 wonderful kids
- My batchmates and fellow graduate students at the LSU Dept. of Chemical Engineering
- The faculty and staff at the LSU Dept. of Chemical Engineering
- My fellow volunteers at Geaux Team of the LSU Athletics Dept.
- My Filipino friends from other universities (Mississippi State, SUNY-Buffalo, Purdue, Houston, Michigan State, Texas A&M, Hawai’i-Manoa, Georgia Tech, North Carolina State, Clemson, Georgetown, Virginia Tech, Cornell, Texas-Dallas)
- The International Hospitality Foundation, the LSU International Services, the LSU International Student Association
- The LSU Graduate School
- The Chapel on the Campus, Starkville Community Church, 220U
- All my former roommates
- All my friends and everyone I came across with

for making my life in graduate school memorable and worthwhile.
## TABLE OF CONTENTS

ACKNOWLEDGMENTS.................................................................ii

ABSTRACT.....................................................................................v

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

CHAPTER 2. REVIEW OF RELATED LITERATURE..............................3
  2.1. Deep Structures in Pre-patterned p-Type Silicon.........................3
  2.2. Principles of Electrochemical Etching.......................................3
  2.3. Silicon-electrolyte Interface..................................................4
  2.4. Physics of Macropore Formation in p-Type Silicon....................6
  2.5. Porous Silicon Formation.....................................................6
  2.6. Linear Sweep Voltammogram...............................................10
  2.7. Mechanism of Silicon Dissolution in Hydrofluoric Acid Solution...12
  2.8. Modulating the Silicon Etching Process................................17
  2.9. Electrochemical Etching in the Presence of Fluoride Complexes...23
  2.10. Chemical Etching...........................................................24
  2.11. Monolayer Patterning of Silicon.........................................25

CHAPTER 3. MATERIALS AND METHODOLOGY..............................26
  3.1. Substrate Preparation........................................................26
  3.2. Electrochemical Etching.....................................................27
  3.3. Chemical Etching............................................................29
  3.4. Solution Preparation........................................................29
  3.5. Passivation...........................................................................29
  3.6. Materials Characterization................................................29

CHAPTER 4. RESULTS AND DISCUSSION.....................................30
  4.1. Space Charge Region (SCR) Effects.......................................30
  4.2. Quantitative Analysis on Etching of Isolated Structures..............35
  4.3. Chemical Etching of Electrochemically-etched p-Type Silicon......43
  4.4. Consequence of SCR: Array Edge Isotropic Etching and Uneven Etching...46
  4.5. Passivation of p-Type Silicon..............................................46

CHAPTER 5. SUMMARY AND CONCLUSION.................................49

CHAPTER 6. RECOMMENDATIONS..............................................50

REFERENCES..............................................................................52

APPENDIX A. SPACE CHARGE REGION (SCR) CALCULATIONS.........56

APPENDIX B. RAW DATA FOR PLOTTING THE EFFECT OF SCR ON FIGURE 4.3 II III AND IV.................................................................58
The role of the space charge region (SCR) was demonstrated in isolated structures for the first time. Electrochemical etching was conducted in differently pitched structures in p-type silicon. A design of experiment was also performed to evaluate the effect of electrolyte and applied potential. Finally chemical etching was demonstrated as a possible post-etch clean to porous structures. The results showed that the morphology of etched structures in pre-patterned silicon is strongly influenced by the SCR even in isolated structures. Using lightly-doped p-type Si (1,000-10,000 Ω-cm), deep macropores were obtained in wide-pitched patterns. However, the diameter of the pores grew larger from its initial opening size. As the pitch increased, sidewall etching became more severe and the ratio of the final pore wall thickness to the pitch decreased, which was expected from SCR effect. The results agreed with Lehmann’s theory which state that if the pore wall thickness is greater than twice the SCR width, sidewall etching takes place. The etched structure can either be porous or electropolished depending on prevailing local etching condition. The results from design of experiment (DOE) meanwhile showed that deep structures are more favored at higher HF concentration and potential. Five out of 18 samples showed 40% better anisotropy than KOH while 4 samples showed etch rates better than 1 μm/min. The mean etch rate in tight pitch structures were only 18.42% higher than in isolated structures. Lastly, chemical etching in 1:3:2 HF:HNO₃:CH₃COOH at 5-10 °C showed success in polishing of porous structures with a high etch rate of up to 5 μm/min. In light with the SCR effects, a design specification for macropore can be tailored by carefully adjusting the doping level of silicon while providing optimum etching condition.
CHAPTER 1. INTRODUCTION

Electrochemical etching in hydrofluoric acid (HF) solution is a well-known technique to fabricate different structures in silicon for a wide range of application such as in the area of photonics, solid state, micro-systems engineering, and biosensors (Astrova et al, 2004). One of the earliest application used densely-spaced macropore arrays following an Ottow technique for used as photonic crystals. Muller et al (2002) demonstrated Brownian pumping by intentionally modulated saw-tooth shaped pore walls. Lehmann and Ronnebeck (1999) fabricated X-ray filters by filling an array of macropores with lead, followed by wet etching of silicon, for used in CCD cameras. Macropores have also been studied for use as chemical microreactors due to its large surface area such as those by Bengtsson et al (2000). Macropores have also been used as biochips where in certain coated biochemical compounds responds with specific DNA sequences. Macropore arrays have also been used as sensors for air quality monitoring. The pore walls are coated with semiconducting SnO₂ film and the film changes its resistivity in response to benzene present in the air. Silicon-on-Insulator were the first large-scale commercial application of porous silicon such as the ingenious Epitaxial layer TRANSfer (ELTRAN™) made by Canon. A large number of electro-luminiscent devices have also been developed (Foll, et al 2002). Pioneering studies began with Uhlir and Ingeborg of Bell Laboratory in 1956 and Turner in 1958 (Hassan, et al 1995, Muller, et al 2010). The formation of macropores was first demonstrated by Propst and Kohl in 1994. Since then, the process was extended to lithographically patterned silicon. Deep smooth anisotropic macropores have been successfully fabricated achieving etch rates of about 1 μm/min. This is commonly achieved on patterns having pitch around the width of the space charge region (SCR) (Starkov, 2003; Vyatkin, et al, 2002; Ohji, et al, 2000). Meanwhile, the role of SCR in isolated structures has not been studied.
In this project, electrochemical etching of isolated structures in p-type Si will be evaluated and explained in terms of the SCR. The effect of other factors on the etching behavior will also be discussed.
CHAPTER 2. REVIEW OF RELATED LITERATURE

2.1 Deep Structures in Pre-patterned p-Type Silicon

Several groups have demonstrated electrochemical etching of deep structures in tightly pitched p-type Si (see Table 2.1). Micrometer-sized macropores were fabricated on p-type Si having resistivity in the range of 1 – 1,000 Ω-cm. The pitches vary from 4 to 24 μm. Hydrofluoric acid was the main etchant mixed with different solvents such as 2-propanol, ethanol, dimethyl formamide, and water. The vertical dissolution etch rate is less than 1.0 μm/min (Starkov, 2003; Vyatkin et al, 2002; Ohji et al, 2000). As will be discussed later, the size and anisotropy of macropore is largely a consequence of the silicon property, specifically its resistivity. Pore formation and etch rate are also dependent on the etching solution.

Table 2.1. Summary of related works on p-type silicon.

<table>
<thead>
<tr>
<th>Group</th>
<th>Resistivity, Ω-cm</th>
<th>Pitch, μm</th>
<th>Via size opening, μm²</th>
<th>FPWT/Pitch %</th>
<th>Etch Rate, μm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohji et al 2000</td>
<td>1-10</td>
<td>4, 6, 10</td>
<td>2</td>
<td>13, 8, 5</td>
<td>0.4-0.6</td>
</tr>
<tr>
<td>Starkov 2003</td>
<td>6 - &gt;1,000</td>
<td>18</td>
<td>14</td>
<td>56</td>
<td>0.3-0.9</td>
</tr>
<tr>
<td>Vyatkin et al 2002</td>
<td>6 - &gt;1,000</td>
<td>24</td>
<td>20</td>
<td>42</td>
<td>0.5-0.8</td>
</tr>
</tbody>
</table>

2.2 Principles of Electrochemical Etching

Electrochemical etching of p-type Si is a complex process which involves understanding the principles of semiconductor device, silicon-electrolyte interface, and electrochemistry. When silicon is immersed in HF solution, a semiconductor-electrolyte interface is formed (Gerischer et al, 1993). This interface has interesting properties. In the succeeding paragraphs, the basic theories of silicon electrochemical etching will be discussed, such as interfacial phenomenon, etching mechanisms, role of electrolyte and potential. The discussion however will focus more on the effect of space charge region (SCR).
Silicon (Si) can be electrochemically etched in hydrofluoric acid (HF) solution to form a stable and soluble silicon hexafluoride ions, SiF$_6^{2-}$,

$$2h^+ + 6HF + Si \rightarrow SiF_6^{2-} + H_2 + 4H^+$$

The process requires an externally applied potential to drive the reaction. Availability of holes is essential in the process. In p-type Si, the substrate is doped with group III elements such as boron (B). Since group III elements have 3 valence electrons, they can form covalent bond with 3 neighboring Si atoms. However, with the fourth Si atom, an electron in the anti-bonding orbital is missing, which is referred to as hole ($h^+$). On the other hand, in n-type Si, the substrate is doped with group V elements such as phosphorus (P) to form Si-dopant bonds that have excess electrons but without missing bonds. For p-type Si, holes are readily available. For n-type Si however, holes may be generated by striking a light source with energy sufficiently greater than the Si band gap of 1.12 eV, from a p-n junction (Kan et al 2007), or with high thermal energy. In this manner, Si-Si bonds can break and release electron-hole pairs (Pierret, 1996). Without an applied potential, Si can also be etched in the presence of a strong oxidizing agent. The oxidizing agent injects holes into Si surface by a reduction step. (Steinert et al, 2007) This will be discussed in more details on the succeeding parts.

### 2.3 Silicon-Electrolyte Interface

When a p-type Si is in contact with an electrolyte, band bending occurs on the Si surface even under zero current potential. Band bending results from equilibration of the Fermi energy level in the silicon side with that of the chemical potential (redox potential) in the electrolyte side. Since for p-type, the Fermi energy level lies closer to the valence band, the valence and conduction band bend downwards. Also, the redox potential of the electrolyte is higher than the
Si Fermi energy (Zhang, 2001). This downward bending pushes the electrons towards the surface. Under anodic bias, holes are pushed towards the interface allowing a nucleophilic attack by ions in the electrolyte (Kolasinski, 2009). Consequently, the existence of charge imbalance results to formation of the SCR. Its width will depend on the applied potential and doping concentration. The higher the doping concentration (or the lower the resistivity), the shorter is the SCR. The width of SCR affects the type of mechanism by which electrons and holes exchange. For example, at shorter SCR, electrons or holes can move by tunneling effect. At the electrolyte side, ions align depending on the charge that lies immediately at the Si surface. The layer in direct contact with the Si surface is the Helmholtz layer. The charge at the Helmholtz layer is opposite to that of the SCR (Tiginyanu et al, 2009).

Figure 2.1. Band bending in a Si-electrolyte interface at equilibrium (zero current potential).
2.4 Porous Silicon Formation

A large number of studies on electrochemical etching of p-type silicon are aimed at fabricating porous structures without masked patterns. The resulting morphology is influenced by several factors which will be discussed more in the succeeding parts. These are electrolyte composition, silicon doping, and anodization. As an example, macropores are usually formed in aqueous HF solution at resistivity above 5 Ω-cm. Lust and Levy-clement (2002) meanwhile have obtained macropores in heavily-doped silicon greater than 0.1 Ω-cm using organic HF solution. Depending on the applied condition, the size of the pores generated can range from a few nanometers to a few micrometers. Lehmann and Ronnebeck (1999) noted that the porosity is weakly dependent on current density while the pore size increases with decreasing doping level. There is also preference in pore growth towards the (100) orientation but not as strongly as with n-type silicon (Lehmann and Ronnebeck, 1999).

2.5 Physics of Macropore Formation in p-Type Silicon

Porous silicon can be classified based on the diameter of the pore. Pores with diameter less than 2 nm are classified as micropores. Pores with diameters between 2 nm and 50 nm are grouped as mesopores. Pores with diameter greater than 50 nm are called macropores (Janshoff et al, 1998). Lehmann and Ronnebeck (1999) discussed macropore formation in p-type Si during electrochemical etching. At zero bias (electrostatic condition), there are no electric field present in the bulk Si. However, at the interface between Si and electrolyte, there exists a SCR in the Si. The width (W) of the SCR was also found to depend on interface geometry. Some values of SCR for different pore pit geometry at doping concentration of $10^{15}$ cm$^{-3}$ and potential of 0.5V is given below,
Table 2.2. Width of SCR at various pore pit geometry \((N_A=10^{15} \text{ cm}^{-3}, V = 0.5V^*)\)

<table>
<thead>
<tr>
<th>Pore pit</th>
<th>SCR width, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>785</td>
</tr>
<tr>
<td>Cylindrical</td>
<td>680</td>
</tr>
<tr>
<td>Hemispherical</td>
<td>590</td>
</tr>
<tr>
<td>Conical</td>
<td>&lt; 590</td>
</tr>
</tbody>
</table>

\( V = (V_{bi} - V_{app}) - 2kT/e \)

The next table provides the theoretical SCR width at zero current potential for different p-type Si wafers. These values have been calculated based on the simplified Poisson equation given by Pierret (1996),

\[
W = \sqrt{\frac{2K \cdot q(V_b - V)}{\varepsilon \cdot N_A}} \quad (2.1)
\]

where \(W\) is the SCR width, \(V\) and \(V_b\) are the applied potential and built-in potential respectively, \(N_A\) is the acceptor concentration, \(K\) is the dielectric constant (11.8), \(\varepsilon\) is the permittivity of free space \((8.85 \times 10^{-14} \text{ farad/cm})\), and \(q\) is the charge of the electron \((1.602 \times 10^{-19} \text{ C})\) (Suemasu et al, 2002). The equation assumes that the electrolyte is heavily-doped and acts like a metal. The built-in potential \((V_b)\) is calculated from the equation,

\[
V_b = \frac{E_G}{2q} + \frac{k \cdot T}{q} \ln \left( \frac{N_A}{n_i} \right) \quad (2.2)
\]

Where \(E_G\) is the Si band gap \((1.12 \text{ eV})\), \(k\) is the Boltzmann constant \(= 8.617 \times 10^{-5} \text{ eV/K}\), \(n_i\) is the intrinsic concentration \(= 8.60 \times 10^9 /\text{cm}^3\) for Si at 25 °C (Pierret, 1996). The built-in potential is
the height of bending at the Si surface. As can be seen, SCR increases with resistivity. For p-type Si (1,000-10,000 Ω-cm), SCR is about 8 μm.

<table>
<thead>
<tr>
<th>Resistivity, Ω-cm</th>
<th>W (at equilibrium), μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>1</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>0.41</td>
</tr>
<tr>
<td>10</td>
<td>0.87</td>
</tr>
<tr>
<td>20</td>
<td>1.26</td>
</tr>
<tr>
<td>40</td>
<td>1.74</td>
</tr>
<tr>
<td>100</td>
<td>2.66</td>
</tr>
<tr>
<td>1,000</td>
<td>7.84</td>
</tr>
<tr>
<td>10,000</td>
<td>23.12</td>
</tr>
</tbody>
</table>

When Si is anodized in HF solution, the electrode is under depletion and acts like a solid-state Schottky diode under forward condition. The forward current of this diode is dictated by either diffusion, thermionic emission, or by tunneling of holes. At zero bias and under forward condition, the SCR is not completely depleted of holes. Hence, there exists a diffusion current ($I_{\text{diff}}$) due to hole concentration gradient, based on Schottky theory. This diffusion current is counter-balanced by electric field current ($I_{\text{field}}$) at zero current potential under thermal equilibrium and are equal but opposite in any parts of the pore pit. However, both $I_{\text{diff}}$ and $I_{\text{field}}$ are stronger at the pore tip than at the pore wall. Once a forward bias, $V_{\text{app}}$, is applied, $I_{\text{diff}}$ increases while $I_{\text{field}}$ decreases. At the pore tip, this change is stronger, e.g. $I_{\text{tip}} = (I_{\text{diff}} - I_{\text{field}})$ is greater than $I_{\text{wall}} = (I_{\text{diff}} - I_{\text{field}})$. Hence, in Si surface that is initially pitted e.g. with KOH, deep macropores can form (Lehmann and Ronnebeck, 1999).
If the distance between pore tips is smaller than twice the SCR width, the pore wall becomes passivated by lack of available holes and no wall etching takes place (Lehmann and Ronnebeck, 1999). At the tip, SCR width is at the minimum, creating a maximum hole concentration gradient (Vyatkin et al, 2002).

The forward current of an anodized Si can be dominated by either diffusion, thermionic emission, or by tunneling of holes, as mentioned. At doping concentration of $10^{15}$ cm$^{-3}$, diffusion is the dominant charge transfer. At higher doping concentrations, such as $10^{17}$ cm$^{-3}$, thermionic emission prevails. Holes acquire enough energy to overcome the potential barrier, creating thermionic emission current. For such cases, holes must have a mean free path that is larger than the SCR width. Consequently, there is no higher current density at the pore tips and no macropores are expected to form. At an even higher doping concentration of $10^{18}$ cm$^{-3}$ ($\rho=0.045$ $\Omega$-cm), hole tunneling is the dominant charge transfer mechanism. According to Lehmann and Ronnebeck (1999), only mesopores can form on Si since SCR widths are in the order of nanometers.
2.6 Linear Sweep Voltammogram

The oxidation of Si in HF solution is characterized by a linear sweep voltammetry such as one shown below,

![Voltammogram](image)


The curve is characterized by a peak which distinguishes between a region of porous silicon formation and electropolishing. The peak is called the critical current density and varies with HF concentration, temperature, hydrodynamics (Meerakker and Mellier, 2001), and type of solvent used. In some solvents, e.g. water and ethanol, more than one peak is present. (Lust and Levy-Clement, 2002). When etching is done at potential below the critical current density, there is no silicon oxide build-up, since any oxide that forms dissolve quickly. At the critical current density, the rate of oxide build up and break down is about the same. Beyond the critical current
density, an oxide forms faster than it is being dissolved, resulting to oxide build up (Ronkel and Schultze, 2000). At the critical potential, the over-all Si dissolution reaction is broken down into two steps, namely, the anodic oxidation of Si to SiO$_2$ followed by the chemical dissolution of SiO$_2$ by HF.

\[
\text{Si} + 2\text{H}_2\text{O} + 2\text{h}^+ \rightarrow \text{SiO}_2 + \text{H}_2 + 2\text{H}^+ \\
\text{SiO}_2 + 6\text{HF} \rightarrow \text{SiF}_6^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+
\]

The peak potential where the critical current density resides is believed to be both diffusion-controlled and kinetics-controlled. It obeys the Koutecky-Levich equation to a large extent for a rotating Si electrode. Both diffusion and kinetic current contributes to the total current. Below the peak current, the kinetics (or charge transfer) is the limiting step. This means that fluoride species are abundant at the interface because they are not consumed as fast as they get diffused towards the interface. Meanwhile, beyond the peak current, diffusion (or mass transfer) is the limiting step. Silicon reacts with water molecules faster than fluoride species, forming oxides that are eventually etched by HF species (Meerakker and Mellier, 2001). Others have used the critical HF concentration to distinguish between mass transfer and charge transfer limiting steps. Below the critical HF concentration, kinetics limit the dissolution process while above the critical HF concentration, diffusion controls the reaction rate (Hassan et al, 1995). Homma, et al (2005) provided a model equation to approximate the critical current density as a function of HF concentration and temperature in n-type Si,

\[
I_{pc} = 3.3000 \times [(\text{HF})^{1.4} \times \exp(-\frac{4004}{T})]
\]
where $J_{ps}$ is the critical current density in mA/cm$^2$, $[HF]$ is HF concentration in wt %, and $T$ is temperature in K.

2.7. Mechanism of Silicon Dissolution in Hydrofluoric Acid Solution

Si can be etched in four different ways, (1) by using HF with applied bias, (2) by using HF in the presence of a strong oxidizing agent, (3) by using HF and a light source under anodic bias (for n-type Si), and (3) by using a base such as KOH and TMAH at elevated temperature.

![Figure 2.4. Schematic illustration of H-termination in <100> and <111> Si crystal plane.](image)

For the first case, the etching of Si is believed to consist of electrochemical (slow step) and chemical (fast step) components. For the <111> plane, where Si is monohydride terminated, the overall reactions are,

\[
\text{Si}_3\text{-Si-H} + \text{HF} + 2h^+ \rightarrow \text{Si}_3\text{-Si-F} + 2H^+ \text{ (slow, electrochemical)}
\]

\[
\text{Si}_3\text{-Si-F} + 5\text{HF} \rightarrow \text{(SiH)}_3 + 2H^+ + \text{SiF}_6^{2-} \text{ (fast, chemical)}
\]
On the other hand, for the \(<100>\) plane, where Si is dihydride terminated, the over-all reactions are, (Outemzabet et al, 2006)

\[
\text{Si}_2\text{-Si-H,H} + \text{HF} + 2h^+ \rightarrow \text{Si}_2\text{-Si-H,F} + 2H^+ \text{ (slow, electrochemical)}
\]

\[
\text{Si}_2\text{-Si-H,F} + 5\text{HF} \rightarrow (\text{SiH})_2 + 2H^+ + H_2 + \text{SiF}_6^{2-} \text{ (fast, chemical)}
\]

Authors suggested the following to occur during Si dissolution in aqueous HF solution. It is certain that \(\text{SiF}_6^{2-}\) is the final form of Si. During anodization, the Si-Si bonds at the surface are weakened by the holes that approach the surface (Rappich, 2004). The presence of hole in the Si-Si bond results to a Si with one electron deficiency, \(\text{Si}^+\). This deficient Si bond enhances H abstraction by \(\text{F}^-\) (Vyatkin et al, 2002). Hydrogen gas evolves in most cases, except when electrolyte uses anhydrous acetonitrile (MeCN) as the solvent. The evolution of \(H_2\) gas is therefore a part of the hydrolysis of etch products but not from the etching process (Kolasinski, 2003). The strong polarization of Si-Si back bonds make them vulnerable to attack by polar molecules such as \(\text{HF}_2^-\) and HF. The ion \(\text{HF}_2^-\) is considered more reactive than HF. Si dissolves as \(\text{SiH}_x\text{F}_y(\text{OH})_z\), where \(x + y + z = 4\). These products are not stable in aqueous solution, hence they eventually transform into the more stable form, \(\text{SiF}_6^{2-}\) by further reaction with \(\text{F}^-, \text{HF}_2^-, \text{HF}, \text{OH}^-, \text{or H}_2\text{O}\) species (Rappich, 2004 and Kolasinski, 2003). The remaining Si-Si back bonds are again hydrogenated (Rappich, 2004). In most cases, the dissolution is controlled by hole diffusion towards the surface. The succeeding steps proceed relatively fast. The various molecules on the interface, such as \(\text{H}_2\text{O}, \text{OH}^-, \text{H}^+, \text{and F}^\), has no impact in this rate determining step. However, they may be involved in other steps. If etching is done in the porous regime, the silicon surface is predominantly H terminated, with rarely physisorbed F and O atoms. This
terminated surface has low reactivity, and molecules such as O₂, H₂O, and HF would have weak sticking coefficient (Kolasinski, 2003). Moreover, H passivation is most favored in <111> plane (Vyatkin et al, 2002). The OH⁻ in H₂O may have high sticking coefficient that is larger than F⁻ and hence may also attack the Si-H bond, depending on the pH. Nonetheless, the sticking coefficient of F⁻ goes up by orders of magnitude as soon as holes drift towards the Si-Si surface bonds. In 12 wt% HF solution, it was shown that at the pH of 8.9, the Si dissolution etch rate initiated by OH⁻ equals that of F⁻. Likewise, the chemical etch rate equals that of the electrochemical etch rate and the resulting etch surfaces move from rough (F⁻ initiated) to smooth (OH⁻ initiated). (Kolasinski, 2003)

Silicon dissolution is not observed when bias is not applied or when light is not illuminated in the case of n-type, unless there is a strong oxidizing agent. Though the process is thermodynamically favored, it is kinetically inert. As mentioned earlier, the Si-H is chemically unreactive. Silicon dissolution however is spontaneous in an alkaline solution (OH⁻) at elevated temperature,

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

Furthermore, silicon dioxide dissolution is spontaneous and proceeds naturally by any of these two reactions,

\[
\text{SiO}_2 + 6\text{HF} \rightarrow \text{SiF}_6^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+
\]

\[
\text{SiO}_2 + 3\text{HF}_2^- \rightarrow \text{SiF}_6^{2-} + \text{H}_2\text{O} + \text{OH}^-
\]
So essentially, $F^-$ and $OH^-$ initiate breakdown of Si-Si bonds and the succeeding steps are quite similar. The $OH^-$ initiated step becomes prevalent at higher pH, at about 8 and up, and creates the characteristic $<111>$ oriented smooth plane. Higher temperature also enhances this anisotropic chemical etch. Presence of hole is not needed. The abstraction of $H^+$ results to $-SiHF_2$ bonds that quickly transforms into $SiH_xF_y(OH)_z$,

\[
\begin{align*}
SiHF_2 + HF_2^- & \rightarrow SiHF_3 + F^- \\
SiHF_2 + HF & \rightarrow SiHF_3 (rnx 1) \\
SiHF_2 + H_2O & \rightarrow SiHF_2OH
\end{align*}
\]

The product of reaction 1 can also be attacked by $H_2O$ in the following manner,

\[
\begin{align*}
SiHF_3 + H_2O & \rightarrow SiF_3OH + H_2 \\
SiF_3OH + HF & \rightarrow SiF_4 + H_2O \\
SiF_4 + 2F^- & \rightarrow SiF_6^{2-}
\end{align*}
\]

Finally, $SiHF_3$ swiftly becomes $SiF_6^{2-}$,

\[
\begin{align*}
SiHF_3 + HF + 2F^- & \rightarrow SiF_6^{2-} + H_2
\end{align*}
\]

The dissolution of Si requires 2 holes per Si atom. (Jakubowicz, 2006) Two more holes participate in the succeeding reactions until the final stable form of $SiF_6^{2-}$ is reached.
In dilute fluoride solution, the concentration of H$_2$O is high compared to HF. This may result in the formation of Si-OH (silanol) instead of Si-F intermediate. If the potential is kept low, this Si-OH will eventually result in Si dissolution. But at high potential, where the flux of holes to the surface is larger, leading to an increase in current density, Si-OH can transform into siloxane bridges, Si-O-Si. Nevertheless, these siloxane bridges will eventually decay into dissolved Si by fluorination. However, further increase in potential may lead to permanent oxide layer formation. This hinders further increase in current density, though current oscillation is likely due to ion transport through the cracks in the oxide layer. (Outemzabet et al, 2006)

Si-H + H$_2$O + 2h$^+$ $\rightarrow$ Si-OH + 2H$^+$

Si-OH + Si-OH $\rightarrow$ Si-O-Si + H$_2$O

Si-O-Si + HF $\rightarrow$ Si-OH + Si-F

Si-OH + HF $\rightarrow$ Si-F + H$_2$O

The substitution of H with F can also be explained with respect to surface states. In the presence of F$^-$ ions, the H terminated surface can have very few spots of Si$^-$ which are stabilized by polar molecules e.g. (HF)$_2$, HF, and H$_2$O. These areas are occupied surface states capable of trapping and detrapping electrons in the conduction band. Emptying these surface states produces a very reactive radical. At very positive potential above open circuit potential (Fermi level sufficiently below the surface state energy), radical formation and etching will be fast. The density of surface state correlate with current density, since the pH at the highest surface state density also coincides with the highest current density. At low pH below where the peak current occurs, a flat behavior of current with pH can be correctly accounted for if all the species, F$, HF,
(HF)$_2$, HF$_2^-$, OH$^-$, and H$_2$O are involved in the etching process. A flat behavior of surface density states with pH can be attributed to occurrences of unaccounted surface states that arises during the chemical etching process. The OH$^-$ has a stronger attacking power than F$^-$ over Si-H because the former is a nucleophile and the latter is an electrophile. (Hoffmann et al, 2000) However, as soon as holes are captured in the vicinity of the interface, the sticking coefficient of F goes up by orders of magnitude. Even though the Si-F bond energy, which is 550 kJ/mol is higher than Si-H, which is 290 kJ/mol, the Si-F bond is unstable due to the high electronegativity of F (electronegativity = 4) that causes Si-Si polarization. Etching is also faster at areas where there are two bulk Si-Si bonds and two Si-H bonds. Each time a Si atom is removed, the number of kink sites increase. (Hoffmann et al, 2000)

2.8. Modulating the Silicon Etching Process

Several factors affect the etching behavior of silicon, namely, (1) potentiometry, (2) pH and electrolyte composition, (3) silicon properties, and (4) whether a design mask is used or not. These have been extensively studied for pore formation but have not been extended into evaluating isolated structures. The effects of these variables are rather complicated.

Potentiometry refers to a supply of current and potential (a.k.a. bias). Potential is the driving force for hole drift and diffusion into the Si-electrolyte interface. Either current or potential affects surface phenomenon on Si such as possible oxide build up and dissolution. It also affects the solution composition. For example, in aqueous HF solution, water begins to oxidize at a potential of -1.763V vs SHE. Bias affects the width of the SCR and the extent of band bending of the conduction and valence bands.
The pH and composition of the etching solution are important variables too. They affect both the etch rate and etch quality. In aqueous HF, pH dictates the species that are present in the solution and their relative amounts. As shown in the diagram of Figure 2.5, the solution is mostly HF and (HF)$_2$ at pH 0-2 with some HF$_2^-$ and few F$^-$. Around pH 3.1, there are equal amounts of HF, (HF)$_2$, and F$^-$, while HF$_2^-$ is slightly dominant. At pH greater than 4.5, F$^-$ ions begin to concentrate while other species approach negligible amounts.

![Figure 2.5. Concentration of species in a 1.0 M NH$_4$F solution buffered by addition of HF as a function of pH. (Reference: P.M. Hoffmann, I.E. Vermeir, P.C. Searson. 2000. “Electrochemical Etching of n-Type Silicon in Fluoride Solutions.” Journal of The Electrochemical Society 147 (8), 2999-3002) (Reproduced with permission from The Electrochemical Society, Inc.)](image)

Matsumura and Fukidome (1996) have observed that the anodic current density and etch rate were highest at about the pH range of 6.0-6.6, with an assumption that one silicon atom is etched by losing four electrons.
According to them, at more acidic pH, HF is predominant, and is believed to keep the Si-H bonds stable. However, at pH 6.4, the HF concentration is very low and physisorbed Si-F bonds could be traced from XPS analysis (Matsumura and Fukidome, 1996). Nonetheless, the role of OH⁻ ions was not incorporated in their study, which is expected to take significant role at high pH. Similarly, Hoffmann et al (2000) explained that at pH beyond the peak of 7, the low anodic current density is attributed to low amounts of HF, HF₂⁻, and the HF dimer. The high current density at peak showed an increase in surface state density (Hoffmann et al, 2000).

It has been shown that Si can also be electrochemically etched in water-free solutions of HF and complex fluoride such as BF₄⁻, PF₆⁻, CF₃SO₃⁻, AsF₆⁻, and SbF₆⁻. These alternative complex fluoride sources do not etch SiO₂ in the absence of HF, whether in aqueous or non-aqueous solution. Likewise, dissolution does not end in H-termination because of their lack of protons, resulting to an increase in surface state density. Consequently, no current multiplication is observed. However, potentiometry data would show current oscillation even at these HF-free systems, which supposedly reflect the build up and dissolution of SiO₂. Others suggest a different route, which includes dielectric breakdown, ion transport through defects in low quality
oxide resulting to dissolution of the underlying surface. While some believe there is no apparent connection between the oscillation observed and the SiO₂ dissolution. Nonetheless, it is clear that the water content in the electrolyte correlates with oxide growth. Formation of silicon dioxide increased with water content and frequency of the oscillation (Reiger et al, 1999).

The properties of Si also affect the etching process as well as the etching quality. For example, n-type Si would require a light source. KOH etching of square pattern in <100> plane leads to formation of inverted pyramidal pits, while etching of <110> plane leads to formation of cubic pits (Hah, 2008). Resistivity of Si is an important etching variable which is determined by the concentration of dopant. As seen in Table 2.4, the higher the doping concentration, the lower the resistivity.

<table>
<thead>
<tr>
<th>Doping Level (atoms/cm³), Boron</th>
<th>Resistivity, Ω-cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10¹²</td>
<td>13,000</td>
</tr>
<tr>
<td>10¹³</td>
<td>1,300</td>
</tr>
<tr>
<td>10¹⁴</td>
<td>130</td>
</tr>
<tr>
<td>10¹⁵</td>
<td>14</td>
</tr>
<tr>
<td>10¹⁶</td>
<td>1.5</td>
</tr>
<tr>
<td>10¹⁷</td>
<td>0.2</td>
</tr>
<tr>
<td>10¹⁸</td>
<td>0.045</td>
</tr>
</tbody>
</table>


The resistivity of Si also affects the width of SCR. The SCR of 100 Ω-cm Si would be about 10x wider than that of 1 Ω-cm Si. The concept of SCR has important consequences as far as etching structures with varying pitches. With wider SCR, holes are farther away from the interface. Holes would have more tendencies to move to the bottom pit since they have no drift path.
towards the sidewall (Vyatkin et al, 2002). The thickness of Si wafer also affects uniformity of etching across the surface. Non-uniform etch depth has been observed with deepest structures near the perimeter of the array. According to Homma et al (2005), this is due to uneven supply of holes, having more on these regions than those on the inner areas of the array. Optimizing the thickness of the silicon substrate was shown to minimize this effect (Homma et al, 2005).

The use of mask and presence of KOH inverted pit also affects the etching process (see Fig. 2.7). Without a patterned mask, electrochemical etching in flat silicon surface generates random pores. Pore formations are more favored in sites that are rough or have weakly bonded Si-Si bonds. Such process is commonly used to fabricate luminescence devices and silicon-on-insulator (Madou, 2002). On the other hand, when silicon is patterned with lithography and KOH, the electric field profile of the silicon surface is modified during anodization, such that etching can be tailored to occur more at the tip of the inverted pyramidal pit. In effect, ordered structures can be obtained (Lehmann and Ronnebeck, 1999).

![Figure 2.7. SEM images showing random macropores (left) and ordered trenches (right).](image-url)
The use of KOH is common in wet etching. It is uniquely selective to specific crystal orientation, resulting to inverted pyramid or V-shaped pits in <100> Si wafer having 54.74° angle with respect to the <100> surface, or box-shaped pits in <110> Si wafer. The etch ratio of Si (100) to Si (111) is 100, while the etch ratio of Si (110) to Si (111) is 5,500. KOH etching can be applied to structures with wide and shallow or deep features, or as an etch initiator. High aspect ratio structures are unobtainable. Nevertheless, it is a low cost process and is compatible with CMOS device fabrication (Feng et al, 2005).

Silicon nitride (Si$_3$N$_4$) is commonly used as mask in wet etching since it is slowly etched in HF. UV lithography is used to pattern the nitride layer using positive photoresist. The nitride etch rate is about 0.0130 μm/min (Du Bois et al, 2001).

Figure 2.8. Diagram illustrating hole-limiting and fluoride-limiting cases.
All these variables affect the etching behavior. The HF concentration, Si resistivity, and applied potential determine whether the reaction is limited by the transport of fluoride ions or by charge transfer through the interface. The surface may have very few fluoride ions such as in dilute solution and with plenty of holes at the interface due to a strong applied potential. Then the dissolution process is mass transfer-limited. The surface may have too much fluoride species but with very few holes to initiate the attack of fluoride ions on the hydride terminated Si-Si bonds. Then the dissolution is charge-transfer limited (Homma et al, 2005).

2.9. Electrochemical Etching in the Presence of Fluoride Complexes

As mentioned, electrochemical etching in F complex molecules such as BF$_4^-$ and PF$_6^-$ is possible. In the presence of BF$_4^-$, Si is oxidized by the following reaction,

$$\text{Si} + 6\text{BF}_4^- + nh^+ \rightarrow \text{SiF}_6^{2-} + 6\text{BF}_3 + (4 - n)e^-$$

The breaking of bonds is attributed to the strong polarization of Si-F surface bonds. However, with BF$_4^-$, there are no HF or free F$^-$ species present. Any free F$^-$ ions easily bonds with BF$_3$ to form BF$_4^-$ ($\text{BF}_4^- \leftrightarrow \text{BF}_3 + \text{F}^-$, $k_{eq} = 10^{-39}$). However, at the Si surface, oxidized Si has the ability to strip off F from BF$_4^-$ creating Si-F surfaces. Hence, the breaking of Si-Si back bonds proceeds similarly except before the occurrences of Si-F surface bonds. H-termination in BF$_4^-$ etching is not sustained and removed during the initial oxidation.

Electrochemical etching in hexafluorophosphate (PF$_6^-$) has not been fully evaluated. Hexafluorophosphoric acid (HPF$_6$) is unstable and forms a truncated octahedral cage of hexahydrate in the framework of H-bonded water molecules, as shown below,
Figure 2.9. The hexahydrate geometry of PF$_6^-$.
Canadian Journal of Chemistry Vol. 50, 3515-3520.) (With Permission from the NRC Research Press)

NMR studies show some HF molecules are also fused into the lattice. The chemical analysis reveals PF$_6^-$ in the form of H$_3$O$^+$PF$_6^-$HF.4H$_2$O. Unlike in BF$_3$ where freely flowing F$^-$ is favorably bonded to form BF$_4^-$, PF$_6^-$ creates strong linkages with HF molecules to form the hexahydrate. Hexafluorophosphate is just one of several fluorophosphates that exist in equilibrium. Some HF also exists in the mixture (Davidson and Garg, 1972). Hexafluorophosphate can be carefully prepared by mixing HF with H$_3$PO$_4$ and H$_2$O. For example, 43% PF$_6^-$ can be obtained by mixing 63% HF with 33% H$_3$PO$_4$ and 4% H$_2$O.

2.10. Chemical Etching

HF/HNO$_3$ etching is an electroless electrochemical process that does not require an external bias to initiate the etching of silicon. The nitric acid, whose electronic energy distribution function overlaps the valence bond of silicon, effectively oxidizes Si by accepting electrons from the latter’s valence bond (Tiginyanu et al, 2009). HF/HNO$_3$ etching has been used in MEMS fabrication to smooth surfaces and remove defects in silicon. The etching
reaction involves silicon dioxide formation by nitric acid, followed by stripping of silicon dioxide by hydrofluoric acid.

$$3 \text{Si} + 4 \text{HNO}_3 \rightarrow 3 \text{SiO}_2 + 4 \text{NO} + 2 \text{H}_2\text{O}$$

$$\text{SiO}_2 + 6 \text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2 \text{H}_2\text{O}$$

$$3 \text{Si} + 4 \text{HNO}_3 + 18 \text{HF} \rightarrow 3 \text{H}_2\text{SiF}_6 + 4 \text{NO} + 8 \text{H}_2\text{O}$$

The etching characteristic was shown to vary between HF-rich mixture and HNO₃-rich mixture. In HF-rich solution, reactive nitrogen intermediates exhibit strong effect on the etch rates and the etching process, while in HNO₃-rich solution, they show minimal effect (Steinert et al, 2007).

2.11. Monolayer Patterning of Silicon

Besides etching, silicon surface can be modified by an electrochemical method. The terminal atoms of silicon which are usually hydrogen can be replaced with functional groups using several methods such as electrografting and by non-electrochemical methods such as photolithography, e-beam lithography, and AFM-based methods. The surface modification allows creating monolayer patterns for subsequent etching or deposition (Vegunta et al, 2010).
CHAPTER 3. MATERIALS AND METHODOLOGY

3.1. Substrate Preparation

Prior to electrochemical etching, bare p-type silicon (Si) wafers with different resistivities were coated with 1.0 μm thick silicon nitride (Si₃N₄) film via low pressure chemical vapor deposition (LPCVD) at the Microelectronics Research Center (MiRC) in Georgia Institute of Technology (GaTech). UV lithography was conducted at the Center for Advanced Microstructures and Devices (CAMD) to create ordered patterns. The patterns were drawn from AutoCAD then flashed into a soda lime glass reticle using Mann 3600 Pattern Generator. The
arrays consisted of squares and trenches of various sizes and pitches. In order to create patterns on the Si$_3$N$_4$ layer, the surface was first spin-coated with 3 µm thick Shipley SC 1800’s photoresist at 2,500-3,000 rpm for 30 seconds. The wafer was then soft-baked at M206 Mechanical Convection Oven at 80-90°C for 30 minutes. Afterwards, the wafer was exposed to ultraviolet light using Oriel UV Exposure Station with Aligner for 15 seconds at a 365 nm wavelength and 100 mW/cm$^2$ light intensity. The photoresist was developed in a 10% Microposit 351 solution for 60 seconds, then hard-baked at 80-90°C for a few minutes.

After UV lithography, the pattern in the photomask was successfully transferred into the Si$_3$N$_4$ layer. With the hard-baked photoresist on the surface, reactive ion etching (RIE) in Oxford PlasmaLab 100 ICP-DRIE System was performed to remove Si$_3$N$_4$ on the open regions. The dry etchant was carbon tetrafluoride (CF$_4$) gas flowing at 30 sccm for 60 minutes. The Si$_3$N$_4$ layer on the backside of the wafer was also removed by RIE. When RIE was completed, the photoresist was removed by immersing the wafer in acetone for several minutes.

After RIE, the wafer was etched in potassium hydroxide (KOH) to create inverted pyramidal pits. The solution consisted of 40 mL of 30% KOH and 6.4 mL of isopropyl alcohol (IPA). Etching was done at 70-80 °C for 10 minutes under stirred condition. Finally, the wafer was cleaved into 12 samples.

3.2. Electrochemical Etching

Etching of pre-patterned p-type Si wafer was done inside an electrochemical cell reactor fabricated at the Chemical Engineering Machine Shop. The reactor was made of Teflon with a volumetric capacity of 10 mL. The wafer was the working electrode placed on top of a brass metal plate with Gallium-Indium (GaIn) eutectic coating in between. The brass electrode which
extends to the bottom of the reactor was connected to the potentiostat via cable wire with alligator clip. The counter electrode and the pseudo-reference electrode, made of platinum (Pt), were fixed to the top of the reactor and were similarly connected to the potentiostat. The etchant solution was poured onto the reactor and was sealed against the backside of the wafer with a viton O-ring. Potentiometry was performed using Princeton Applied Research Potentiostat/Galvanostat Model 263A. The wafer was pre-cleaned in a 10% hydrofluoric acid (HF) solution for a few minutes to remove native silicon dioxides (nSiO₂) then rinsed in H₂O. After electrochemical etching, the wafer was rinsed in H₂O and prepared for material characterization such as Scanning Electron Microscopy (SEM).

Figure 3.2. Electrochemical cell set-up (top) and diagram (bottom).
3.3. Chemical Etching

Ex situ chemical etching was also done at some Si wafers after electrochemical etching. The electroless etchant consisted of HF, nitric acid (HNO$_3$), and acetic acid (CH$_3$COOH) at a ratio of 1:3:2. The HF concentration was 10%. The etching time varied from 30-120 s depending on the etch structure obtained from electrochemical etching. The temperature was kept between 5-10 °C. The wafer was rinsed in H$_2$O afterwards.

3.4. Solution Preparation

The etchant for Si etching was HF in 2-propanol ((CH$_3$)$_2$CHOH) solution at various compositions. A design of experiment was created to study the effect of electrolyte and potential.

3.5. Passivation

Methyl termination of Si surface was performed by electrografting in 3M methyl magnesium chloride (CH$_3$MgCl) with tetrahydrofuran (C$_4$H$_8$O) at a constant potential of 0.1 V vs Ag/AgCl for 2 minutes. Electrografted samples were then rinsed in de-ionized H$_2$O and sonicated in IPA and toluene (C$_6$H$_5$CH$_3$). In another sample, the surface was passivated with octadecyltrichlorosilane (C$_{18}$H$_{37}$Cl$_3$Si) in toluene (1:10 v/v). Si wafer was dipped for a few minutes, then rinsed with 2-propanol and ethanol (CH$_3$CH$_2$OH).

3.6. Materials Characterization

Characterization of electrochemically etched silicon was largely done by taking images from an SEM to evaluate etch profile and rates.
CHAPTER 4. RESULTS AND DISCUSSION

4.1. Space Charge Region Effects

A few groups have demonstrated the role of space charge region (SCR) in p-type Si with different resistivities. Those who studied highly resistive substrate considered pitches near the SCR. In this work, electrochemical etching of both tightly pitched and isolated structures were conducted in lightly doped p-type Si (1,000-10,000 Ω·cm) to determine the effects of SCR in isolated structures. Different opening sizes and pitches were considered. For each experiment, the pore wall thickness before and after etching was measured. The ratio of the final pore wall thickness (FPWT) to pitch and the ratio of the FPWT to SCR width were calculated and plotted against pitch or pitch/SCR ratio in Figure 4.3. The SEM images of the etched structures used in the calculation are shown in Figure 4.1 except for “e” and “f.” The SEM images are arranged in increasing pitch from top left to bottom right until in “e”.

Figure 4.1. SEM images showing SCR effects on p-type Si (1,000-10,000 Ω·cm), (a) initial trench width = 6 μm, initial pitch = 20, (b) initial via opening size = 8 μm, initial pitch = 30 μm, (c) initial trench width = 30 μm, initial pitch = 60 μm, (d) initial via opening size = 15 μm, initial pitch = 100 μm, (e) initial via opening size = 50 μm, initial pitch = 500 μm, (f) KOH initial pit.
When silicon is in contact with an electrolyte, band bending at the silicon side of the interface gives rise to a layer of depleted carriers called the SCR. Depletion is due to electrons and holes migrating and recombining during equilibration. The movement of carriers across the interface and into the bulk of the silicon leaves the SCR in a charge state. The length of the SCR, which is dependent on doping and applied potential can be estimated from the equation,

\[ W = \sqrt{\frac{2N_A e (V_b - V)}{q N_A}} \]  

where \( W \) is the SCR width, \( V \) and \( V_b \) are the applied potential and built-in potential respectively, \( N_A \) is the acceptor concentration, \( K \) is the dielectric constant (11.8), \( e \) is the permittivity of free space (8.85 x 10^{-14} \text{ farad/cm}) and \( q \) is the charge of the electron (1.602 x 10^{-19} \text{ C}) (Suemasu et al, 2002). For p-type 1,000-10,000 \( \Omega \)-cm Si, the theoretical SCR width is about 8 \( \mu \text{m} \).

Figure 4.2. Diagram illustrating Lehmann’s statement on role of SCR.

Figure 4.2 illustrates Lehmann’s statement about the effect of SCR. The one on the left has pore wall thickness that is exactly twice the SCR. Notice that no holes are present at the
middle pore wall. Likewise, no holes can diffuse. On the other hand, the one on the right shows pore wall thickness that is greater than twice the SCR. Holes will be available and side etching will occur. Following up from Lehmann and Ronnebeck (1999), deep anisotropic macropores in some p-type Si (usually lightly doped) can therefore be fabricated with diameters about equal to the opening size if the distance between pore initiators is about twice the SCR width. However, for pitches greater than twice the SCR, widening of the diameter is expected. This is exactly what the SEM results have showed. As the pitch increases, the extent of lateral etching also increases due to presence of field paths for holes to reach on the side. This etching will continue until the pore wall thickness reaches the vicinity of the SCR since all missing bonds have been used up in the reaction by this time. Etching in the pore tip continues since holes are present in the bulk of the substrate. However, there must be sufficient HF molecules to prevent any build-up of oxide. The etch rate will decrease with depth due to mass transfer effects, (Vytakin, et al, 2002) coupled with a decrease in fluoride species and an increase in the concentration of silicon hexafluoride ions ($\text{SiF}_6^{2-}$) and other by-products. In tightly pitched structures such as in Figure 4.1a, no significant sidewall etching and widening of macropore is observed since the structures are closely packed. The pore walls immediately reached a depleted state. Figure 4.3 shows pitch effects quantitatively. A drawing is provided to aid with the argument.

![Figure 4.3](image)

Figure 4.3. Graphs showing pitch effects on deep macropore formation in p-type silicon, (I) drawing to aid the argument, (II) FPWT/Pitch vs Pitch, (III) FPWT/Pitch vs Pitch/SCR, (IV) FPWT/SCR vs Pitch/SCR.
(Fig. 4.3 cont’d)

II

(Fig. 4.3 cont’d)

III

33
As shown in Figure 4.3 (II), the previous works of two groups on highly resistive substrates have focused on pitches about twice the SCR width. Ohji et al (2000) meanwhile worked on 1-20 Ω-cm wafers and considered pitches up to seven times greater than the SCR (see Figure 4.3 (III)). Based on Lehmann’s statement, if the initial pore wall thickness (or pitch) is greater than twice the SCR, the FPWT after etching will be less than the initial one. Since for any pitch, the FPWT will always be around twice the SCR, then the ratio of the FPWT to pitch will decrease with increasing pitch. Such is the case shown in Figure 4.3 (II). The first two data points are about the same as that of Starkov (2003) and Vyatkin et al (2002). Additionally, the same SCR behavior was observed for wider pitches, as the ratio of the FPWT to pitch continued to decrease with pitch. Normalizing the pitch to SCR (Figure 4.3 (III)), a parallel behavior can also be observed with p-type 10-20 Ω-cm. Since its SCR is less than that of p-type 1,000-10,000 Ω-cm, anisotropy will occur at a tighter pitch. In strong agreement with Lehmann’s theory, all of
the data points from this work and previous literature have FPWT to SCR ratio that does not exceed two, the limit value according to Lehmann and Ronnebeck (1999) (see Figure 4.3 (IV)). However, most of these data also fell well below two. It is common with structures at pitch of less than 10 μm. Hence, the FPWT to SCR ratio can be regarded as an electrochemical threshold. Meaning, any further etching below the ratio of two is chemical in nature. Kobayashi et al (2007) meanwhile suggested this behavior to positional relation of the pores.

The presence of SCR was demonstrated to be a major controlling variable during electrochemical etching. Etching will occur in all exposed Si surface in the KOH pit for an isolated pitch greater than twice the SCR. The bottom pit and the KOH plane crevices will be more favored sites due to presence of highly-strained Si-Si bonds. Etching can be deep or shallow, depending on other factors. In lieu of this, the design objectives can be tailored by carefully considering the doping concentration, besides the electrolyte composition and potential. For example, if the design goal is to fabricate deep structures that are 20 μm apart, a p-type Si with resistivity around 2,000 Ω-cm would be suitable to use. Wider pitch would require even more resistive substrate. However, it is important to keep in mind that modulating the doping level also changes the conductivity of silicon.

4.2. Quantitative Analysis on Etching of Isolated Structures

A design of experiment (DOE) was performed to assess the effect of electrolyte and potential on deep trench formation. The variables studied were HF concentration (1%, 5.5%, and 10%), IPA concentration (0%, 40%, 80%), and applied potential (0.0V and 4.0V). The responses were relative anisotropy (anisotropy vs. KOH) and etch rate. Isolated trenches with 6 μm width and 500 μm pitch were drawn into silicon substrate by UV lithography and were used to facilitate SEM imaging. The results of the DOE are presented in Table 4.1. The anisotropy and
etch rates were averaged for each parameter and are tabulated in Table 4.2. The mean etch rates in tightly pitched and isolated structures are compared. Finally, the marginal means plot are constructed for each parameter.

Table 4.1. Full factorial design of experiment.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>HF</th>
<th>IPA</th>
<th>Potential (vs NHE)</th>
<th>Anisotropy data for t = 1 hr</th>
<th>Vertical Etch Rate (μm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Absolute Anisotropy</td>
<td>Anisotropy vs KOH</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1.44</td>
<td>1.02</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>4</td>
<td>1.45</td>
<td>1.03</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>40</td>
<td>0</td>
<td>1.48</td>
<td>1.05</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>40</td>
<td>4</td>
<td>1.26</td>
<td>0.89</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>80</td>
<td>0</td>
<td>1.61</td>
<td>1.14</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>80</td>
<td>4</td>
<td>1.49</td>
<td>1.06</td>
</tr>
<tr>
<td>7</td>
<td>5.5</td>
<td>0</td>
<td>0</td>
<td>1.68</td>
<td>1.19</td>
</tr>
<tr>
<td>8</td>
<td>5.5</td>
<td>0</td>
<td>4</td>
<td>2.24*</td>
<td>1.59</td>
</tr>
<tr>
<td>9</td>
<td>5.5</td>
<td>40</td>
<td>0</td>
<td>1.95*</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.09*</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.16*</td>
<td>1.53</td>
</tr>
<tr>
<td>10</td>
<td>5.5</td>
<td>40</td>
<td>4</td>
<td>2.10**</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.34</td>
<td>5.91</td>
</tr>
<tr>
<td>11</td>
<td>5.5</td>
<td>80</td>
<td>0</td>
<td>1.64</td>
<td>1.16</td>
</tr>
<tr>
<td>12</td>
<td>5.5</td>
<td>80</td>
<td>4</td>
<td>1.81</td>
<td>1.28</td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>2.02</td>
<td>1.43</td>
</tr>
<tr>
<td>14</td>
<td>10</td>
<td>0</td>
<td>4</td>
<td>1.88</td>
<td>1.33</td>
</tr>
<tr>
<td>15</td>
<td>10</td>
<td>40</td>
<td>0</td>
<td>1.92</td>
<td>1.36</td>
</tr>
<tr>
<td>16</td>
<td>10</td>
<td>40</td>
<td>4</td>
<td>37.40</td>
<td>26.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.53**</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.07</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.49**</td>
<td>1.06</td>
</tr>
<tr>
<td>17</td>
<td>10</td>
<td>80</td>
<td>0</td>
<td>1.60</td>
<td>1.13</td>
</tr>
<tr>
<td>18</td>
<td>10</td>
<td>80</td>
<td>4</td>
<td>1.80**</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Data reported in small font were not used during regression analysis.

* rough, ** porous or highly-branched

Anisotropy relative to KOH is calculated by dividing anisotropy with the anisotropy of KOH which is 1.41. In this respect, any relative anisotropy values that are greater than 1.00 will
have better anisotropy than KOH. Based on the Tables and plots, 5 out of 18 samples showed 40% better anisotropy than KOH.

Table 4.2. Group mean data showing effect of variables on relative anisotropy and etch rate in isolated structures.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Anisotropy vs KOH</th>
<th>Etch Rate, μm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF concentration, (v/v) %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.03</td>
<td>0.08</td>
</tr>
<tr>
<td>5.5</td>
<td>1.39 (1.89)</td>
<td>0.47 (0.55)</td>
</tr>
<tr>
<td>10.0</td>
<td>1.27 (4.07)</td>
<td>0.83 (0.97)</td>
</tr>
<tr>
<td>IPA concentration, (v/v) %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.27</td>
<td>0.22</td>
</tr>
<tr>
<td>40</td>
<td>1.28 (3.77)</td>
<td>0.79 (0.94)</td>
</tr>
<tr>
<td>80</td>
<td>1.18</td>
<td>0.30</td>
</tr>
<tr>
<td>Potential vs NHE, V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.26</td>
<td>0.18</td>
</tr>
<tr>
<td>4</td>
<td>1.23 (2.80)</td>
<td>0.81 (0.94)</td>
</tr>
<tr>
<td>Sample 16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% HF, 40% IPA, 4V</td>
<td>1.21 (7.54)</td>
<td>1.69 (1.79)</td>
</tr>
<tr>
<td>Sample 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.5% HF, 40% IPA, 4V</td>
<td>1.49 (3.70)</td>
<td>0.98 (1.10)</td>
</tr>
</tbody>
</table>

Data in () includes the 2 extreme values of relative anisotropy in sample 10 and 16.

There was no appreciable etching observed in samples etched with 1% HF solution reflecting a low mean etch rate value of 0.08 μm/min. However, with increased HF at the interface, such as in 5.5% and 10% HF, etching is hastened. Deep anisotropic trenches were formed in sample 10 (5.5% HF, 40% IPA, 4V vs NHE) and 16 (10% HF, 40% IPA, 4V vs NHE). The highest etch rate is found from sample 16, at 2.70 μm/min while averaging at 1.69 μm/min across the substrate. The structure of this particular trench however is porous and isotropic (see Table 4.4). Four samples showed etch rates greater than one μm/min compared to previous results. Consistent with past literature, higher HF concentration increases the etch rate. This is because at higher HF concentration, more species of fluoride are available to etch the silicon.
Etching however must be under kinetics limitation. Meanwhile, anisotropy reached a high of 26.53 measured from another trench but at the same substrate that also showed the highest etch rate. Another trench showed anisotropy of 5.91. Some input data have more than one value. This is a result of uneven etching that may be attributed to presence of varying mechanical stress across the wafer or could also be due to uneven distribution of the electrolyte species. The effect of stress has not been studied. The structures that showed very high anisotropy were omitted in the regression analysis but are likewise reported for their importance. Based on regression analysis, potential was shown to be the only significant factor with respect to etch rate with p-value of 0.03 at 95% confidence level. On the other hand, the HF concentration was the only significant factor with respect to relative anisotropy, with p-value of 0.02 at 95% confidence level.

Defining anisotropy in a structure is pitch-dependent. In tightly pitched structures, etching can be anisotropic right from the beginning. However, in moderately pitched structures, etching will be isotropic initially. With extended time, the etching can become anisotropic. In widely pitched structures, the time frame under isotropic condition will be longer. But anisotropic etching is still possible. Anisotropy and etch rate are not dependent on each other. A structure fabricated at a high rate can be isotropic or anisotropic.

From the marginal means plots in Figure 4.4, the effect of potential on anisotropy and etch rate are directly proportional. For HF, the effect on anisotropy is highest at 5.5% while the effect on etch rate is proportional. For IPA, anisotropy is more favored at lower concentration while the etch rate is highest at the intermediate concentration of 40%. These relationships are valid for a given range. At a much elevated potential, other reactions will begin to affect the etching process. The highest etch rate was obtained when the concentration of IPA and water are
Figure 4.4. Marginal means plot of HF, IPA, and potential and their effect on relative anisotropy and etch rate.

about the same. Water is an aprotic solvent. It solvates ions effectively by hydrogen bonding. As a result, etching ions are stabilized and are less reactive. Isopropyl alcohol on the other hand is a protic solvent and holds ions only by weak dispersion forces. Hence, etching ions especially
smaller ones like $F^-$ can easily break Si-Si bonds (Lust and Levy-Clement 2002) However, IPA can also act as a passivating solvent since it forms complexes with silicon intermediates (Nayfeh et al, 2009). The role of solvent is difficult to understand. Though they don’t have direct impact on macropore formation, they can influence the quality of macropores formed.

Table 4.3. Etch rate comparison between isolated and tight pitch trenches.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Etch rate, μm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tight Pitch</td>
</tr>
<tr>
<td>HF concentration, (v/v) %</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>IPA concentration, (v/v) %</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>80</td>
</tr>
<tr>
<td>Potential vs NHE, V</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Over-All</td>
<td>NA</td>
</tr>
<tr>
<td>Sample 16</td>
<td>10% HF, 40% IPA, 4V</td>
</tr>
<tr>
<td>Sample 10</td>
<td>5.5% HF, 40% IPA, 4V</td>
</tr>
</tbody>
</table>

The tendency to form deep structures is found to be not strongly affected by pitch. Both isolated and tightly pitched structures showed the ability to form deep trenches. Mean etch rate data showed a difference of 18.42%. Hence the extent of etching is likely dictated by local conditions. The synergy of two factors determines whether silicon will be etched or not; namely, (1) holes diffusing from the bulk of the silicon to the interface and (2) relative sticking coefficient of water and fluoride species at the silicon electrolyte interface (SEI). Some areas of the structure can have higher amount of available holes and this can result to higher volumetric
dissolution rate. In areas of the substrate with high stress level, etching can also proceed rapidly. In areas of the silicon where no appreciable etching occurs, there is rapid oxide build up in the interface such that oxide stripping by HF is insufficient. This is true at higher bias. Though holes may still be drawn to the interface, the aggressiveness of hydroxide termination will hinder the ability of the hole to initiate the abstraction by fluoride ions.

Table 4.4. SEM Images of notable results including anisotropy (vs KOH) and etch rate.

<table>
<thead>
<tr>
<th>SEM Image</th>
<th>Sample</th>
<th>Anisotropy vs KOH</th>
<th>Etch rate, μm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 (1% HF, 40% IPA, 4V)</td>
<td>0.89</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>8 (5.5% HF, 0% IPA, 4V)</td>
<td>1.59</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>9 (5.5% HF, 40% IPA, 0V)</td>
<td>1.53</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>10 (5.5% HF, 40% IPA, 4V)</td>
<td>1.49</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.91</td>
<td>1.22</td>
</tr>
</tbody>
</table>
Notable results were selected from a pool of SEM images and are presented in Table 4.4. Except for sample 4, the rest of the structures have depth of more than 50 μm, which is a good threshold for through silicon trenches (TST) in 3D interconnect technologies. Majority of them however are isotropic and either porous or rough. On these samples, chemical etching can be applied. However, there are few structures from sample 10 that would be an excellent fit for a TST. So far, TST have not been under consideration for 3D Interconnect. But this result provides electrochemical etching with a strong consideration as alternative to BOSCH. Copper deposition and process integration have not been performed.
4.3. Chemical Etching of Electrochemically Etched p-Type Silicon

Chemical etching is a viable post-etch clean that provides a method to smooth rough surfaces or fix any surface defects obtained after electrochemical etching. The etching is primarily initiated by a strong oxidizing agent such as HNO₃, in place of an externally applied bias. With chemical etching in place, electrochemical etching can be done on a wider operating condition. As mentioned earlier, the etching behavior of silicon in an HF containing electrolyte is a complicated phenomenon. The tendency for porous formation or electropolishing still remains vague, with no clear line separating the two morphologies, since the critical current density is not a fix value. It differs for any given combination of etching variable. Deep electropolished structures have also been obtained. For these cases, no further post etch clean is needed. However, for deep porous structures, chemical etching can be applied. Either way, a smooth etched structure can be achieved.

Figure 4.5. Time evolution of electroless electrochemical etching of p-type 10-20 Ω-cm in 1:3 HF:HNO₃ 10% HF. 5-10 °C, (a) 2 min, (b) 6 min.
Figure 4.6. Electrochemical etching followed by chemical etching of p-type Si (1,000-10,000 Ω-cm) in 10% HF, 40% IPA, at 4.0 V, (a) before post etch clean, (b) after post etch clean in 10% HF, 1:3 HF:HNO₃.

Figure 4.5 and 4.6 show how an electrochemically etched surface can be cleaned by chemical etching. Various compositions have been considered with HNA, using those formulas that were used by related research works. The HNA composition suitable for post etch clean was found to be 1:3 HF:HNO₃ with 10% HF and temperature within 5-10 °C. In this way, formations of nitrogen-containing intermediates that can influence the etching process are avoided. Since chemical etching is not influenced by the presence of KOH pit and holes from bulk Si, the electrolyte tends to smooth a surface spherically. With chemical etching, there is no preference towards the pit. Reaction proceeds immediately in any area of contact without regards to crystal orientation.

KOH etching is crystal orientation dependent. It is usually used to etch structures that do not require high aspect ratio. The etch rate is about 0.75 – 1.25 μm/min, for etching in a 30% KOH solution at 70-80 °C temperature. The etch rate increases with temperature but decreases at
higher KOH concentration. Using a KOH concentration of less than 30%, the etched surface is often rough. The addition of IPA enhance surface smoothness but reduces the etch rate by about 20% (Seidel et al, 1990). On the other hand, chemical etching is not crystal orientation dependent. Etching propagates radially from any open surface. It is mainly used to smooth rough surface that resulted from electrochemical etching. Using HNO₃ as the oxidizing agent, relatively high etch rates could be achieved. For the case of 10% HF in 1:3 HF:HNO₃ (v/v) at 5-10 °C, an etch rate as high as 5 μm/min was reached. Meanwhile, electrochemical etching had etch rate as high as 3 μm/min demonstrated from an isolated structure using 10% HF solution. Chemical etching will always approach a very smooth surface regardless of the initial roughness of the surface. However for very rough surfaces, making them smooth sacrifices the desired macropore dimension. Table 4.5 provides a brief comparison between electrochemical etching, chemical etching, and KOH etching.

<table>
<thead>
<tr>
<th>Property</th>
<th>Chemical Etching</th>
<th>KOH Etching</th>
<th>Electrochemical Etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Application</td>
<td>To smooth surfaces and fix surface defects</td>
<td>To fabricate trenches and vias</td>
<td>To fabricate porous structures</td>
</tr>
<tr>
<td>Etching direction</td>
<td>Radial</td>
<td>Crystal orientation dependent</td>
<td>Electric field dependent; Random (for unpatterned Si)</td>
</tr>
<tr>
<td>Etch rate</td>
<td>Up to 5 μm/min</td>
<td>About 1 μm/min</td>
<td>Up to 3 μm/min</td>
</tr>
<tr>
<td>Strength</td>
<td>High etch rate</td>
<td>Controlled anisotropy</td>
<td>Good control</td>
</tr>
<tr>
<td>Weakness</td>
<td>Difficult to control, poor anisotropy</td>
<td>Opening size dependent; Low aspect ratio</td>
<td>Requires an external current source</td>
</tr>
</tbody>
</table>

Table 4.5. Comparison of ex situ chemical etching, electrochemical etching, and KOH etching.
4.4. Consequence of Space Charge Width: Array Edge Isotropic Etching and Uneven Etching

The etching behavior on array edges follows the consequence of space charge width. As shown in Figure 4.7, on one side, etching is restricted due to the presence of a neighboring structure. However, on the other side, etching is very aggressive and propagates orthogonally with the KOH surface. The reason is the availability of more holes at the edges. The concentration of holes that is at the core would be less than that at the edges of the array. At the edges, additional holes are present at the bulk on left or right. At the core, there is higher demand towards lesser available holes. Hence, on the average, etching is faster at the edges.

Figure 4.7. SEM showing sidewall etching on the array edge and uneven depth. p-type Si (1,000-10,000 Ω-cm) etched in (a) 10% HF 40% IPA at 4.0V vs NHE (pitch = 100 μm, via initial size = 40 μm), (b) 11% HF 39% IPA at 4.0V potential vs NHE (pitch = 30 μm, via initial size = 8 μm)

4.5. Passivation of p-Type Silicon

An in-situ passivation of KOH pit was done to study the effect of monolayers on electrochemical etching of p-type 40-100 Ω-cm. Passivation may allow deep etching without sidewall growth caused by SCR. The passivating compound is octadecyltrichlorosilane in
toluene (1:10 v/v). Silicon sample was dipped for a few minutes and then rinsed with isopropanol and ethanol. The octadecyltrichlorosilane/toluene layer on the KOH surface showed some effect on etching activity in the sidewall. The passivating layer withstood few minutes of HF etching. Hence, we see a non-uniform porosity on the (111) surfaces. Though the KOH walls were largely covered by the passivating layer, a few open dents triggered pore formation. It caused uneven hole diffusion towards the surface producing differently sized pores.

![Figure 4.8](image1.png)

**Figure 4.8.** Effect of in-situ passivation in p-type Si (40-100 Ω-cm), etched in 10:10:80 HF:H₂O:IPA (a) no passivation, (b) with passivation.

![Figure 4.9](image2.png)

**Figure 4.9.** Effect of methyl termination in p-type Si (40-100 Ω-cm), etched in 10:10:80 HF:H₂O:IPA (a) no methyl termination, (b) with methyl termination.
Figure 4.9 shows significant difference in the resulting structure of p-type Si (40 – 100 Ω-cm) after electrochemical etching in IPA-rich 10% HF solution. The one without methyl termination (left) showed aggressive sidewall etching while the one that is methyl terminated (right) showed inhibited sidewall etching. The methyl group bonded to the (111) plane withstood few minutes of etching before sidewall etching started to occur.
CHAPTER 5. SUMMARY AND CONCLUSION

The effect of space charge region (SCR) in electrochemical etching extends to isolated structures (pitch up to 500 μm) in p-type Si. Though the etching process is a complicated phenomenon, the morphology of the etch structure can be explained largely by SCR effects. Deep structures have been fabricated in both tightly pitched and isolated patterns for very resistive p-type Si wafers (1,000-10,000 Ω-cm). Majority of isolated patterns etched at higher HF concentration and potential showed widening of diameter in structures which were either porous or electropolished. The results agree with Lehmann’s statement that if the pore wall thickness to SCR ratio is greater than two, there will be sidewall etching. SCR effects were demonstrated for the first time in pitches ranging from 50 to 500 μm. Five out of 18 samples showed 40% better anisotropy than KOH, with the highest at about 27x better, while the etch rate is at the high of 2.70 μm/min measured from another trench. Chemical etching meanwhile provides surface polishing of porous structures. Consistent with previous works, doping concentration largely affect both the ability to fabricate deep structures and desired via size. In order to control depth and diameter of micrometer-sized macropores, it is necessary to choose the appropriate doping level as well as pick the right pitch that will meet the design objective.
CHAPTER 6. RECOMMENDATIONS

Majority of the results obtained from the experiment reflect the consequence of space charge region. However, some suggest other potential underlying factors. The highly anisotropic trench obtained from sample 16 was fabricated at a high rate of 2.10 μm/min (see Figure 6.1). After an hour of etching, no side wall etching was observed and all etching was concentrated at the pore tip. Moreover, appreciable amount of HF species were able to diffuse at the interface in such depth despite etching in unstirred condition. As mentioned, highly strained Si-Si bonds are susceptible to nucleophilic attack due to their instability. It is possible that during etching, silicon experienced isolated spots of high mechanical stress due to the electrochemical set-up. Hence, it is interesting to quantitatively study how stress affects the etching behavior of silicon.

Figure 6.1. Deep anisotropic trench fabricated from p-type Si (1,000-10,000 Ω-cm) using 10% HF, 40% IPA at 4.0V vs NHE.

The stress in silicon may have also resulted from low pressure chemical vapor deposition (LPCVD) of silicon nitride (Si₃N₄). Figure 6.2 shows p-type Si (10-20 Ω-cm) from two different sources having different LPCVD recipe. Both samples were etched at the same condition. The one on the left showed a very porous structure while the one on the right showed few scattered
pores. Silicon nitride creates stress in silicon because of differences in the coefficient of thermal expansion between the two materials. After the high temperature LPCVD process, Si$_3$N$_4$ will exhibit a tensile stress with Si creating a curved surface. Understanding the role of silicon nitride LPCVD is important so that the electrochemical etching can be better controlled to meet a specific fabrication goal.

Figure 6.2. Electrochemical etching of blank p-type Si 10-20 $\Omega$-cm from two different sources.
REFERENCES


D. Hah. 2008. EE 7240 Integrated Circuit Engineering Lecture Notes, Dept. of Electrical and Computer Engineering, LSU.


J. Jakubowicz. 2006. “Electrochemical Dissolution of (100) and (111) Oriented n-Type Silicon in HF-containing Electrolytes.” Archives of Materials Science Vol. 27 No. 1, 37-47.


APPENDIX A. SPACE CHARGE REGION (SCR) CALCULATIONS

Space Charge Width (W),

\[ W = \sqrt{\frac{2K \varepsilon (V_b - V)}{q N_A}} \]

Built-in Potential (\(V_b\)),

\[ V_b = \frac{E_G}{2q} + \frac{kT}{q} \ln \left( \frac{N_A}{n_i} \right) \]

Constants

- Permittivity, \(K = 11.8\)
- Permittivity of free space, \(\varepsilon = 8.85 \times 10^{-14}\) Farad/cm
- Temperature, \(T = 300\) K
- Si Band Gap, \(E_G = 1.12\) eV
- Electron charge, \(q = 1.602 \times 10^{-19}\) C
- Boltzmann constant, \(k = 8.617 \times 10^{-5}\) eV/K
- Intrinsic concentration, \(n_i = 8.60 \times 10^9\) /cm³

Conversion: \(1\) eV = \(1.602 \times 10^{-19}\) J

Table A. Built-in Potential and SCR Calculation.

<table>
<thead>
<tr>
<th>Resistivity, (\rho) ((\Omega)-cm)</th>
<th>Doping, (N_A) (atoms/cm³)</th>
<th>Built-in Potential, (V_b) (V)</th>
<th>SCR width, (W) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>9.00 E18</td>
<td>1.09791</td>
<td>0.01</td>
</tr>
<tr>
<td>0.02</td>
<td>3.70 E18</td>
<td>1.07489</td>
<td>0.02</td>
</tr>
<tr>
<td>0.1</td>
<td>2.50 E17</td>
<td>1.00510</td>
<td>0.07</td>
</tr>
<tr>
<td>1</td>
<td>1.50 E16</td>
<td>0.93223</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>7.10 E15</td>
<td>0.91286</td>
<td>0.41</td>
</tr>
<tr>
<td>10</td>
<td>1.50 E15</td>
<td>0.87259</td>
<td>0.87</td>
</tr>
<tr>
<td>20</td>
<td>7.00 E14</td>
<td>0.85285</td>
<td>1.26</td>
</tr>
<tr>
<td>40</td>
<td>3.60 E14</td>
<td>0.83563</td>
<td>1.74</td>
</tr>
<tr>
<td>100</td>
<td>1.50 E14</td>
<td>0.81296</td>
<td>2.66</td>
</tr>
<tr>
<td>1000</td>
<td>1.60 E13</td>
<td>0.75499</td>
<td>7.84</td>
</tr>
<tr>
<td>10000</td>
<td>1.70 E12</td>
<td>0.69692</td>
<td>23.12</td>
</tr>
</tbody>
</table>
Figure A1. Plot of doping concentration ($N_a$) vs. resistivity ($\rho$).

Figure A2. Plot of resistivity ($\rho$) vs. built-in potential ($V_b$).

Figure A3. Plot of resistivity ($\rho$) vs. SCR width.
### APPENDIX B. RAW DATA FOR PLOTTING THE EFFECT OF SCR ON FIGURE 4.3 II III AND IV

Table B. Raw Data for Plotting the Effect of SCR on Figure 4.3 II, III and IV.

<table>
<thead>
<tr>
<th>Pitch</th>
<th>IPWT</th>
<th>FPWT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bugayong (2010), 1,000-10,000 Ω-cm, SCR ~ 7.84 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>30</td>
<td>22</td>
<td>12</td>
</tr>
<tr>
<td>60</td>
<td>30</td>
<td>16</td>
</tr>
<tr>
<td>100</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>Ohji et al (2000), 1-10 Ω-cm, SCR ~ 0.58 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
<td>0.5</td>
</tr>
<tr>
<td>Starkov (2003), &gt; 1,000 Ω-cm, SCR ~ 7.84 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>Vyatkin et al (2002), &gt; 1,000 Ω-cm, SCR ~ 7.84 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>4</td>
<td>10</td>
</tr>
</tbody>
</table>
### APPENDIX C. REGRESSION ANALYSIS

Table C. Raw Data for Design of Experiment Regression Analysis.

<table>
<thead>
<tr>
<th>HF</th>
<th>log HF</th>
<th>IPA</th>
<th>Potential</th>
<th>Overpotential</th>
<th>Log Overpotential</th>
<th>Rel Aniso</th>
<th>Etch Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.24</td>
<td>0.0934</td>
<td>1.02</td>
<td>0.025</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>5.24</td>
<td>0.7193</td>
<td>1.03</td>
<td>0.004</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>40</td>
<td>0</td>
<td>1.24</td>
<td>0.0934</td>
<td>1.05</td>
<td>0.03</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>40</td>
<td>4</td>
<td>5.24</td>
<td>0.7193</td>
<td>0.89</td>
<td>0.283</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>80</td>
<td>0</td>
<td>1.24</td>
<td>0.0934</td>
<td>1.14</td>
<td>0.083</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>80</td>
<td>4</td>
<td>5.24</td>
<td>0.7193</td>
<td>1.06</td>
<td>0.07</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1.24</td>
<td>0.0934</td>
<td>1.43</td>
<td>0.057</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>0</td>
<td>4</td>
<td>5.24</td>
<td>0.7193</td>
<td>1.33</td>
<td>0.065</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>40</td>
<td>0</td>
<td>1.24</td>
<td>0.0934</td>
<td>1.36</td>
<td>0.152</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>40</td>
<td>4</td>
<td>5.24</td>
<td>0.7193</td>
<td>1.21</td>
<td>1.69</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>80</td>
<td>0</td>
<td>1.24</td>
<td>0.0934</td>
<td>1.13</td>
<td>0.024</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>80</td>
<td>4</td>
<td>5.24</td>
<td>0.7193</td>
<td>1.28</td>
<td>1.296</td>
</tr>
<tr>
<td>5.5</td>
<td>0.74</td>
<td>0</td>
<td>0</td>
<td>1.24</td>
<td>0.0934</td>
<td>1.19</td>
<td>0.081</td>
</tr>
<tr>
<td>5.5</td>
<td>0.74</td>
<td>0</td>
<td>4</td>
<td>5.24</td>
<td>0.7193</td>
<td>1.59</td>
<td>1.085</td>
</tr>
<tr>
<td>5.5</td>
<td>0.74</td>
<td>40</td>
<td>0</td>
<td>1.24</td>
<td>0.0934</td>
<td>1.46</td>
<td>0.475</td>
</tr>
<tr>
<td>5.5</td>
<td>0.74</td>
<td>40</td>
<td>4</td>
<td>5.24</td>
<td>0.7193</td>
<td>1.49</td>
<td>0.982</td>
</tr>
<tr>
<td>5.5</td>
<td>0.74</td>
<td>80</td>
<td>0</td>
<td>1.24</td>
<td>0.0934</td>
<td>1.16</td>
<td>0.102</td>
</tr>
<tr>
<td>5.5</td>
<td>0.74</td>
<td>80</td>
<td>4</td>
<td>5.24</td>
<td>0.7193</td>
<td>1.28</td>
<td>0.082</td>
</tr>
<tr>
<td></td>
<td>df</td>
<td>SS</td>
<td>MS</td>
<td>F</td>
<td>Significance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>----</td>
<td>-------------</td>
<td>-------------</td>
<td>---------</td>
<td>--------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regression</td>
<td>3</td>
<td>0.227197222</td>
<td>0.075732407</td>
<td>2.784909442</td>
<td>0.079604028</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>14</td>
<td>0.380713889</td>
<td>0.027193849</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>17</td>
<td>0.607911111</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard</th>
<th>Coefficients</th>
<th>Error</th>
<th>t Stat</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
<th>Lower 95.0%</th>
<th>Upper 95.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>1.089036669</td>
<td>0.09853698</td>
<td>11.15354532</td>
<td>2.377856-08</td>
<td>0.887695868</td>
<td>1.310377471</td>
<td>0.887695868</td>
<td>1.310377471</td>
</tr>
<tr>
<td>HF</td>
<td>0.028703704</td>
<td>0.010578698</td>
<td>2.713349468</td>
<td>0.016811207</td>
<td>0.000014654</td>
<td>0.051392754</td>
<td>0.000014654</td>
<td>0.051392754</td>
</tr>
<tr>
<td>IPA</td>
<td>-0.001125</td>
<td>0.001190103</td>
<td>0.945295944</td>
<td>0.36053793</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log Overpot</td>
<td>0.039054273</td>
<td>0.124198821</td>
<td>0.314449628</td>
<td>0.797816807</td>
<td>0.227325703</td>
<td>0.305434249</td>
<td>0.227325703</td>
<td>0.305434249</td>
</tr>
</tbody>
</table>

Figure C1. Regression Analysis for Relative Anisotropy.
SUMMARY
OUTPUT –
Etch Rate

**Regression Statistics**

| Multiple R | 0.622207895 |
| R Square   | 0.387142664 |
| Adjusted R Square | 0.255816092 |
| Standard Error | 0.450754886 |
| Observations  | 18          |

**ANOVA**

<table>
<thead>
<tr>
<th></th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>3</td>
<td>1.796886972</td>
<td>0.598962324</td>
<td>2.947938549</td>
<td>0.06931184</td>
</tr>
<tr>
<td>Residual</td>
<td>14</td>
<td>2.844520806</td>
<td>0.203180058</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>17</td>
<td>4.64160778</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Coefficients**

<table>
<thead>
<tr>
<th></th>
<th>Standard Error</th>
<th>t Stat</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
<th>Lower 95.0%</th>
<th>Upper 95.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.273157908</td>
<td>0.269342225</td>
<td>1.014166671</td>
<td>0.327710665</td>
<td>0.850839524</td>
<td>0.304523709</td>
<td>0.304523709</td>
</tr>
<tr>
<td>HF</td>
<td>0.051648148</td>
<td>0.028915946</td>
<td>1.78614763</td>
<td>0.095743648</td>
<td>0.010370387</td>
<td>0.113666684</td>
<td>0.113666684</td>
</tr>
<tr>
<td>IPA</td>
<td>0.000708333</td>
<td>0.003253044</td>
<td>0.217744781</td>
<td>0.830769649</td>
<td>0.006288752</td>
<td>0.007685419</td>
<td>0.007685419</td>
</tr>
<tr>
<td>Log Overpot</td>
<td>0.803807846</td>
<td>0.339486625</td>
<td>2.367716094</td>
<td>0.032834758</td>
<td>0.075681554</td>
<td>1.531934337</td>
<td>1.531934337</td>
</tr>
</tbody>
</table>

**Figure C2. Regression Analysis for Etch Rate.**
APPENDIX D. APPROVED PERMISSIONS FOR REUSE OF PUBLISHED MATERIALS

Anne Clementson

From: Joel Bugayong [bugay1@tigers.lsu.edu]
Sent: Saturday, September 18, 2010 3:29 AM
To: Copyright
Subject: Request for Permission to Reproduce or Republish ECS Material
Attachments:
- ECS Lust et al 2002 Chemical Limitations of Macropore Formation on Medium Doped p Type Silicon.pdf
- ECS Hoffmann et al 2000 Electrochemical etching of n type silicon in fluoride solutions.pdf
- ECS Matsumura et al 1996 Enhanced Etching Rate of Silicon in Fluoride Containing Solutions at pH 6.4.pdf
- ECS Vyatkin et al 2002 Random and Ordered Macropore Formation in p Type Silicon.pdf

Follow Up Flag: Follow up
Flag Status: Flagged

To Whom It May Concern:

Good morning. I am requesting permission to reproduce or republish ECS material for the following journal articles.

Figure 1

Figure 3

Figure 2 and 3

Figures 4 and 8

Attached are the filled up forms.

Thank you and have a great day!

Respectfully,

Joel
Request for Permission to Reproduce or Re-Publish ECS Material

Please fax this form to: The Electrochemical Society (ECS), Attn: Permissions Requests, 1.609.730.0629.
You may also e-mail your request to: copyright@electrochem.org. Include all the information as required on this
form. Please allow 3-7 days for your request to be processed.

I am preparing a (choose one):  □ paper  □ chapter  □ book  □ thesis

entitled: ELECTROCHEMICAL ETCHING OF ISOLATED STRUCTURES IN P-TYPE SILICON

to be published by: N/A

in an upcoming publication entitled: N/A

I request permission to use the following material in the publication noted above, and request nonexclusive
rights for all subsequent editions and in all foreign language translations for distribution throughout the world.

Description of material to be used—Indicate what material you wish to use (figures, tables, text, etc.) and give
the full bibliographic reference for the source publication. You may attach a separate list, organized by ECS title.

FIGURES

5. Lust, C. Levu-Clement, “Chemical Limitations of Macropore Formation on
Medium-Doped p-Type Silicon,” J. of Electrochemical Society, 149 (6)
C338-C344, 2002

Signature: ___________________________ Date: SEPT 17, 2010

Name: JOEL NINO E BUGAYONG

Address: W209 CHEMICAL ENG’G BLDG

SOUTH STADIUM DRIVE

BATON ROUGE, LA, 70803

Telephone: 225-578-1416 Fax: ___________________________

E-mail: jbugay1@tigers.lsu.edu

Permission is granted to reproduce the above-referenced material. Please acknowledge the author(s) and
publication data of the original material, and include the words “Reproduced by permission of The
Electrochemical Society.”

Sept. 27, 2010

Date

Ann F. Goedkoop, Director of Publications

63
Request for Permission to Reproduce or Re-Publish ECS Material

Please fax this form to: The Electrochemical Society (ECS), Attn: Permissions Requests, 1.609.730.0629. You may also e-mail your request to: copyright@electrochem.org. Include all the information as required on this form. Please allow 3-7 days for your request to be processed.

I am preparing a (choose one): □ paper  □ chapter  □ book  □ thesis
entitled: ELECTROCHEMICAL ETCHING OF ISOLATED STRUCTURES IN P-TYPE SILICON

to be published by: N/A

in an upcoming publication entitled: N/A

I request permission to use the following material in the publication noted above, and request nonexclusive rights for all subsequent editions and in all foreign language translations for distribution throughout the world.

Description of material to be used—Indicate what material you wish to use (figures, tables, text, etc.) and give the full bibliographic reference for the source publication. You may attach a separate list, organized by ECS title.

FIGURES


Signature: ____________________________ Date: SEPTEMBER 18, 2010

Name: JOEL NINO E BUGAYONG

Address: W207 CHEMICAL ENG BLDG

SOUTH STADIUM DRIVE

BATON ROUGE, LA 70802

Telephone: 225-578-1416 Fax: 

E-mail: jbugay1@tigerslsu.edu

Permission is granted to reproduce the above-referenced material. Please acknowledge the author(s) and publication data of the original material, and include the words: "Reproduced by permission of The Electrochemical Society."

Sept. 27, 2010

Date

Ann F. Goedkoop, Director of Publications
Request for Permission to Reproduce or Re-Publish ECS Material

Please fax this form to: The Electrochemical Society (ECS), Attn: Permissions Requests, 1.609.730.0629. You may also e-mail your request to: copyright@electrochem.org. Include all the information as required on this form. Please allow 3-7 days for your request to be processed.

I am preparing a (choose one): ☐ paper ☐ chapter ☐ book ☑ thesis

entitled: ELECTROCHEMICAL ETCHING OF ISOLATED STRUCTURES IN P-TYPE SILICON
to be published by: N/A

in an upcoming publication entitled: N/A

I request permission to use the following material in the publication noted above, and request nonexclusive rights for all subsequent editions and in all foreign language translations for distribution throughout the world.

Description of material to be used—Indicate what material you wish to use (figures, tables, text, etc.) and give the full bibliographic reference for the source publication. You may attach a separate list, organized by ECS title.

FIGURES


Signature: Date: SEPT 18, 2010

Name: JOEL NINO E BUGAYONG
Address: W202 CHEMICAL ENG BLDG
       SOUTH STADIUM DRIVE
       BATON ROUGE, LA 70803

Telephone: 225-548-1416 Fax: E-mail: jbugayong@tigers.lsu.edu

Permission is granted to reproduce the above-referenced material. Please acknowledge the author(s) and publication data of the original material, and include the words: "Reproduced by permission of The Electrochemical Society."

Date: SEPT 27, 2010
Ann F. Goedkoop, Director of Publications
Request for Permission to Reproduce or Re-Publish ECS Material

Please fax this form to: The Electrochemical Society (ECS), Attn: Permissions Requests, 1.609.730.0629. You may also e-mail your request to: copyright@electrochem.org. Include all the information as required on this form. Please allow 3-7 days for your request to be processed.

I am preparing a (choose one): ☐ paper ☐ chapter ☐ book ☐ thesis

entitled: ELECTROCHEMICAL ETCHING OF ISOLATED STRUCTURES IN P-TYPE SILICON

to be published by: N/A

in an upcoming publication entitled: N/A

I request permission to use the following material in the publication noted above, and request nonexclusive rights for all subsequent editions and in all foreign language translations for distribution throughout the world.

Description of material to be used—Indicate what material you wish to use (figures, tables, text, etc.) and give the full bibliographic reference for the source publication. You may attach a separate list, organized by ECS title.

FIGURES


Signature: ☐

Date: SEPT 18, 2010

Name: JOEL NIND E. BUGAYONG

Address: W209 CHEMICAL ENG BLDG

SOUTH STADIUM DRIVE

BATON ROUGE, LA 70803

Telephone: 225-578-1416 Fax:

E-mail: jbugay1@tigers.lsu.edu

Permission is granted to reproduce the above-referenced material. Please acknowledge the author(s) and publication data of the original material, and include the words: "Reproduced by permission of The Electrochemical Society."

Date: Sept. 27, 2010

Ann F. Goodkoop, Director of Publications
SPRINGER LICENSE
TERMS AND CONDITIONS

This is a License Agreement between Joel Bugayong ("You") and Springer ("Springer") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Springer, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number: 2511501451099
License date: Sep 17, 2010
Licensed content publisher: Springer
Licensed content publication: Journal of Porous Materials
Licensed content title: Electrochemical Aspects of Porous Silicon Formation
Licensed content author: F. Ronkel
Licensed content date: Jan 1, 2000
Volume number: 7
Issue number: 1
Type of Use: Thesis/Dissertation
Portion: Figures
Author of this Springer article: No
Order reference number:
Title of your thesis / dissertation: Electrochemical Etching of Isolated Structures in p-Type Silicon
Expected completion date: Dec 2010
Estimated size(pages): 100
Total: 0.00 USD

Terms and Conditions

Introduction
The publisher for this copyrighted material is Springer Science + Business Media. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.rightslink.com).

Limited License
With reference to your request to reprint in your thesis material on which Springer Science and Business Media control the copyright, permission is granted, free of charge, for the use
indicated in your enquiry. Licenses are for one-time use only with a maximum distribution
equal to the number that you identified in the licensing process.

This License includes use in an electronic form, provided it is password protected or on the
university's intranet, destined to microfilming by UMI and University repository. For any
other electronic use, please contact Springer at (permissions.dordrecht@springer.com or
permissions.heidelberg@springer.com)

The material can only be used for the purpose of defending your thesis, and with a maximum
of 100 extra copies in paper.

Although Springer holds copyright to the material and is entitled to negotiate on rights, this
license is only valid, provided permission is also obtained from the (co) author (address is
given with the article/chapter) and provided it concerns original material which does not
carry references to other sources (if material in question appears with credit to another
source, authorization from that source is required as well). Permission free of charge on this
occasion does not prejudice any rights we might have to charge for reproduction of our
copyrighted material in the future.

Altering/Modifying Material: Not Permitted

However figures and illustrations may be altered minimally to serve your work. Any other
abbreviations, additions, deletions and/or any other alterations shall be made only with prior
written authorization of the author(s) and/or Springer Science + Business Media. (Please
contact Springer at permissions.dordrecht@springer.com or
permissions.heidelberg@springer.com)

Reservation of Rights

Springer Science + Business Media reserves all rights not specifically granted in the
combination of (i) the license details provided by you and accepted in the course of this
licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment
terms and conditions.

Copyright Notice:

Please include the following copyright citation referencing the publication in which the
material was originally published. Where wording is within brackets, please include
verbatim.

"With kind permission from Springer Science + Business Media: <book/journal title,
chapter/article title, volume, year of publication, page, name(s) of author(s), figure
number(s), and any original (first) copyright notice displayed with material>.
"

Warranties: Springer Science + Business Media makes no representations or warranties with
respect to the licensed material.

Indemnity

You hereby indemnify and agree to hold harmless Springer Science + Business Media and
CCC, and their respective officers, directors, employees and agents, from and against any
and all claims arising out of your use of the licensed material other than as specifically
authorized pursuant to this license.

No Transfer of License
This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without Springer Science + Business Media's written permission.

No Amendment Except in Writing
This license may not be amended except in a writing signed by both parties (or, in the case of Springer Science + Business Media, by CCC on Springer Science + Business Media's behalf).

Objection to Contrary Terms
Springer Science + Business Media hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and Springer Science + Business Media (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC’s Billing and Payment terms and conditions, these terms and conditions shall control.

Jurisdiction
All disputes that may arise in connection with this present License, or the breach thereof, shall be settled exclusively by the country's law in which the work was originally published.

Other terms and conditions:

v1.2

Gratis licenses (referencing $0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLK10850968. Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006

If you find copyrighted material related to this license will not be used and wish to cancel, please contact us referencing this license number 2511501451099 and noting the reason for cancellation.

Questions? customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.
NRC RESEARCH PRESS LICENSE
TERMS AND CONDITIONS

Jan 23, 2011

This is a License Agreement between Joel Bugayong ("You") and NRC Research Press ("NRC Research Press") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by NRC Research Press, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number 2595070578384
License date Jan 23, 2011
Licensed content publisher NRC Research Press
Licensed content publication Canadian Journal of Chemistry
Licensed content title The Hydrate of Hexafluorophosphoric Acid
Licensed content author D. W. Davidson and S. K. Garg
Licensed content date Nov 1, 1972
Volume number 50
Issue number 21
Type of Use Thesis/Dissertation
Requestor type Author (original work)
Format Print and electronic
Portion Figure/table
Number of figures/tables 1
Order reference number
Title of your thesis / dissertation Electrochemical etching of isolated structures in p-type silicon
Expected completion date Apr 2011
Estimated size (pages) 75
Total 0.00 USD
Terms and Conditions

General Terms & Conditions

Permission is granted upon the requester's compliance with the following terms and conditions:

1. A credit line will be prominently placed in your product(s) and include: for books the author, book title, editor, copyright holder, year of publication; for journals the author, title of article, title of journal, volume number, issue number, and the inclusive pages. The credit line must include the following wording: "© 2008 NRC Canada or its licensors. Reproduced with permission," except when an author of an original article
published in 2009 or later is reproducing his/her own work.

2. The requester warrants that the material shall not be used in any manner that may be
derogatory to the title, content, or authors of the material or to National Research
Council Canada, including but not limited to an association with conduct that is
fraudulent or otherwise illegal.

3. Permission is granted for the term (for Books/CDs-Shelf Life; for Internet/Intranet-In
perpetuity; for all other forms of print-the life of the title) and purpose specified in
your request. Once term has expired, permission to renew must be made in writing.

4. Permission granted is nonexclusive, and is valid throughout the world in English and
the languages specified in your original request. A new permission must be requested
for revisions of the publication under current consideration.

5. National Research Council Canada cannot supply the requester with the original
artwork or a "clean copy."

6. If the National Research Council Canada material is to be translated, the following
lines must be included: The authors, editors, and National Research Council Canada
are not responsible for errors or omissions in translations.

v1.3

Gratis licenses (referencing $0 in the Total field) are free. Please retain this printable
license for your reference. No payment is required.

If you would like to pay for this license now, please remit this license along with your
payment made payable to "COPYRIGHT CLEARANCE CENTER” otherwise you will be
invoiced within 48 hours of the license date. Payment should be in the form of a check
or money order referencing your account number and this invoice number
RLNK10918775.
Once you receive your invoice for this order, you may pay your invoice by credit card.
Please follow instructions provided at that time.

Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006

If you find copyrighted material related to this license will not be used and wish to
cancel, please contact us referencing this license number 2595070578384 and noting
the reason for cancellation.

Questions? customercare@copyright.com or +1-877-622-5543 (toll free in the US) or
+1-978-646-2777.
VITA

Joel Nino G Bugayong was born in Cebu City, Philippines in 1981. He obtained his undergraduate degree in chemical engineering from the University of the Philippines Los Banos in 2004 where he graduated *magna cum laude*. While in college, he participated in a study abroad program and spent a semester at Michigan State University East Lansing in 2002. He worked at the Institute of Chemistry, University of the Philippines Los Banos from 2004 to 2007 as a laboratory instructor. He later pursued further studies in chemical engineering at Louisiana State University Baton Rouge in 2007 and received the Phi Kappa Phi Fellowship Award of Excellence. He is a lifetime member of the Honor Society of Phi Kappa Phi. Joel enjoys traveling, sports, adventures, photography, and music during his free time.