Two-Photon 3-Dimensional Photoelectrochemical Etching of Single Crystal Silicon Carbide

Peter Robert Nyholm
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Two-Photon 3-Dimensional Photoelectrochemical Etching of Single Crystal Silicon Carbide

Peter R. Nyholm

A thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of
Master of Science

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ABSTRACT

Two-Photon 3-Dimensional Photoelectrochemical Etching of Single Crystal Silicon Carbide

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Master of Science

This thesis presents the first use of a novel direct-write, non-line-of-sight, two-photon photoelectrochemical etching technique for etching of single crystal silicon carbide substrates. The use of this technique has resulted in structuring of 3-dimensional structures in high quality single crystal silicon carbide wafers. The 3-dimensional structures demonstrated cannot be formed by any single or combination of traditional silicon carbide machining techniques. This thesis outlines the development of the optical, electrical, and diagnostic components required to achieve two-photon photoelectrochemical etching in silicon carbide. The diagnostic sub-assemblies—a single pixel confocal detector assembly and an in-situ optical microscope assembly—and their design is also discussed. Several etched structures using the two-photon photoelectrochemical etching technique are presented.

Keywords: two-photon absorption, silicon carbide, photoelectrochemical etching, 3-dimensional etching
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CHAPTER 1. INTRODUCTION

Microelectromechanical systems (MEMS) devices have been an area of increasing interest over the last several decades. The use of these devices is directed towards measurement and sensing of various environmental factors. Silicon (Si) MEMS devices have been well studied and used in many industrial applications including automotive, aerospace, and consumer electronics. However, the mechanical performance of Si begins to degrade at 500°C. This makes Si MEMS devices unsuitable for extreme temperature applications. Because of this, research is being done to replace MEMS sensing devices with materials that demonstrate better thermal and mechanical characteristics.

Silicon carbide (SiC) has long been known as an attractive material for MEMS applications in extreme environments. The mechanical, thermal, and chemical properties of SiC make it ideal for a variety of harsh sensing conditions, as compared to Si. SiC demonstrates a high Young’s modulus and low mass density, making it ideal for resonant devices [1]. The high thermal conductivity, low thermal expansion coefficient, and sublimation temperature of around 2700°C also make SiC suitable for cryogenic and extreme temperature operation [2]. SiC is also well suited for corrosive environment operations due to its inertness to virtually all known chemicals at room-temperature. However, the high hardness of SiC, coupled with its chemical inertness, make it difficult to machine. This limitation, along with the inability to grow large, high quality SiC substrates, has slowed the adoption of SiC into MEMS applications.

Studies within the last two decades have shown an increasing ability to machine MEMS devices from single crystal and polycrystalline SiC substrates. These single crystal and polycrystalline SiC substrates have increased mechanical and thermal characteristics, due to their higher quality, than their amorphous and sintered SiC counterparts. Advances in reactive ion etching (RIE), chemical vapor deposition (CVD), wafer bonding techniques, and lithography have all made use of higher quality SiC possible in MEMS applications.
Rapid increase in the use of SiC in the electronics industry has increased availability of SiC substrates. Figure 1.1 shows a typical SiC wafer used in industry. Because electronics applications require high purity SiC crystals, processes have been developed to form large, single crystal SiC wafers. The most used process to grow high quality SiC wafers is chemical vapor deposition (CVD). The invention and development of CVD has greatly increased the production rate of SiC substrates.

![Figure 1.1: Two SiC wafers.](image)

Many research groups have demonstrated the ability to form MEMS devices from high quality SiC. A variety of resonator devices, such as that shown in Figure 1.2, have been fabricated using a combination of CVD, RIE, and lithography techniques [3]–[6]. Pressure sensors have also been demonstrated using similar techniques, with an additional mechanical milling step in some cases [7]–[10]. Fabrication of a SiC strain sensor using lithography and wafer bonding techniques has also been reported [11]. Placidi et al. has shown that 3C-SiC on silicon substrates may be used to make cantilever structures via wet etch [12]. Hossain et al. [13] has achieved 2.5D structuring of SiC with an undercut etch rate in excess 1µm/hr using metal masking layers and RIE. Many of the techniques used to form these devices can be generally grouped into two groups commonly known as wet etching and dry etching.
Due to the high hardness of SiC, as well as its inertness to virtually all known chemicals at room temperature, it is difficult to machine. While wet and dry etching methods are capable of removing bulk material from SiC, they are limited to surface profile etching. To overcome this limitation, combinations of wet and dry techniques, masking and sacrificial layering, wafer bonding, and epitaxial growth of SiC films have been used to make non surface profile features such as cantilevers, diaphragms, and bridges. In the majority of these cases, a thin SiC layer is suspended over a silicon oxide layer or some other sacrificial etch layer. This means that the device contains silicon oxide and silicon, in addition to single crystal SiC, meaning it would still not be suitable for high temperature or corrosive sensing applications.

The ability to form undercut or suspended structures entirely from single crystal SiC would be a large step forward in MEMS development. Devices formed from solid SiC would be suitable for harsh environment sensing applications. To date, only one method has shown the ability to make undercut SiC from a single SiC bulk. This was done by growing n-type SiC on a p-type SiC substrate, and then electrochemically etching away the p-type substrate underneath the patterned n-type structure [14]–[17]. This type of etching may be thought of as a dopant selective electrochemical etch.

Electrochemical etching of singly doped single crystal SiC has previously been demonstrated [18]–[20]. Etching of n-type SiC was performed with hydrofluoric acid and concurrent illumination by ultraviolet light due to its photon energy exceeding the bandgap energy of the SiC substrate under etch, thus supplying electron holes to the HF interface. Further, p-type SiC has an excess of electron holes due to its doping and thus may be electrochemically etched without additional generation of holes by UV illumination.
While combinations of the etching techniques mentioned have the ability to form 2.5-dimensional structures, none of them can form fully 3D structures in single crystal SiC. The ability to form arbitrary 3D structures in the SiC bulk would provide a large platform for harsh environment sensing applications using single crystal SiC substrates. A direct write, non line-of-sight wet etching technique would be an ideal method to form 3D structures in single crystal SiC substrates.

One research group has shown the possibility of etching fully 3D structures using a non line-of-sight wet etching technique in Si substrates by generating localized volumes of carriers using two photon absorption in the Si bulk with a band-edge (1030nm) Yb-doped femtosecond fiber laser [21]. Results of these experiments yielded high surface roughness near the etch site due to carrier generation by linear absorption and subsequent etching in the material. Application of this same procedure with sub-bandgap light for SiC substrates can be expected to yield similar results, but without excessive surface roughening due to linear absorption as observed when a band-edge illumination source is used.

While sub-bandgap light cannot directly generate holes, a high optical intensity of sub-bandgap light can produce holes through means of two-photon absorption. Generation of localized carriers by means of two photon absorption in SiC substrates would provide a direct write, non line-of-sight wet etching method to make fully 3D structures from single crystal substrates. Applications for this technology include a variety of standard MEMS functions, including through-wafer vias, microfluidic channels, resonant structures, and harsh or corrosive environment sensing. Not only will this method of etching make 3D patterning possible, it will also reduce the complexity of doing so to use of a single tool, greatly reducing tooling times required to manufacture parts.

1.1 Contributions

The following lists the contributions that I have made to research in 3D PEC etching of single crystal silicon carbide substrates at BYU. The major contributions listed relate directly to research performed to develop 3D PEC etching, including papers that I was first author on. Minor contributions are also listed for completeness.
Major Contributions

• Pioneered novel 3D PEC etching technique for surface relief structures in SiC.

• Pioneered novel 3D PEC etching technique for 3D undercut structures in SiC.

• Designed, constructed, and aligned a single pixel confocal microscope system for surface detection of SiC substrates.

• Implemented in-situ optical microscope for surface detection and imaging of etched substrates.

Minor Contributions

• Developed procedures for imaging of subsurface 3D structures in SiC, including FIB and SEM imaging, optical microscope imaging techniques, and confocal fluorescence microscopy techniques.

• Selected, assembled, and aligned all optical components for 3D PEC etching in Si and SiC.

• Retrofitted 3-axis stage with stepper motors and drives with encoder feedback to ensure proper movement in each stage axis.

• Developed surface transform script for making axial adjustments in wafer position to account for variation surface position due to motor cross-talk and substrate pitch and yaw.

• Carried out experimental design for characterization of etch parameters including dwell time, bias voltage and HF concentration for 3D PEC etching.

• Developed and modeled new experimental chamber design for increased user safety, electrolyte cycling, and use of a high numerical aperture objective.
CHAPTER 2. THEORY OF PEC ETCHING

2.1 Photoelectrochemical Etching and Two-Photon Absorption

2.1.1 Photoelectrochemical Etching

At room temperature SiC is a highly chemically resistant material. Many studies have been performed to develop wet and dry etching methods for SiC. Wet etching of SiC has been demonstrated by several researchers [18]–[20]. Wet etching of SiC is generally argued to be a two step electrochemical process. This two step process consists of oxidation of the SiC surface with subsequent oxide etching by hydrofluoric (HF) acid. For silicon oxide to form, electron holes must be present in the SiC substrate as shown by

\[
\begin{align*}
\text{SiC} + 2 \text{H}_2\text{O} + 4 h^+ &\rightarrow \text{SiO} + \text{CO} + 4 \text{H}^+ \\
\text{SiC} + 4 \text{H}_2\text{O} + 8 h^+ &\rightarrow \text{SiO}_2 + \text{CO}_2 + 8 \text{H}^+
\end{align*}
\]

(2.1)

where \( h^+ \) are holes. Generation of the holes in SiC is typically carried out through application of a bias voltage or UV illumination [22]–[24]. In each case, enough energy must be delivered to the atoms in SiC that their electrons cross the band-gap of the material, which will be discussed later. Removal of the oxide is then carried out by a reaction with HF as shown in

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

(2.2)

Others argue that the etching of SiC does not require oxide formation and is a single step process. The reaction taking place in the proposed single step process is

\[
\begin{align*}
\text{SiC} + \text{H}_2\text{O} + 6 \text{F}^- + 6 h^+ &\rightarrow \text{SiF}_6^{2-} + \text{CO} + 2 \text{H}^+ \\
\text{SiC} + 2 \text{H}_2\text{O} + 6 \text{F}^- + 8 h^+ &\rightarrow \text{SiF}_6^{2-} + \text{CO}_2 + 4 \text{H}^+
\end{align*}
\]

(2.3)
Despite the differences in the two-step and single step processes, in each case holes must be present in the substrate and HF must be available to interact with the holes. The requirement of holes and HF make the wet etching process electrochemical in nature.

Several studies have been carried out to demonstrate the ability to electrochemically etch SiC by generating holes in the SiC bulk with light. The use of light to generate holes, coupled with the required electrochemical reaction to etch, is generally called photoelectrochemical (PEC) etching. Shor et al. showed that creation of a porous SiC layer using UV illumination with subsequent 1150°C thermal oxidation and an HF dip could be used to create mesa structures [19]. Rysy et al. also created oxidized SiC surfaces at a SiC-HF interface and later removed the oxidized layer by HF dip to form patterned structures [20]. Shishkin et al. investigated unpatterned photoelectrochemical etching of SiC to form porous SiC layers and proposed that oxidation of the SiC was not required for removal of material, but that HF reacted directly with the SiC bulk and electron–holes to remove material [18].

All studies of SiC wet etching have shown that holes must be present in SiC for electrochemical etching to occur. At room temperature the hole concentration in SiC is low, resulting in resistance to etching in HF. To generate holes in a semiconductor material, an electron must acquire sufficient energy to be excited from the valence band to the conduction band. The energy required for an electron to be excited to the conduction band can be supplied by application of electrical currents, heat, or illumination. Since application of electrical currents or heat is difficult to confine within specific regions of a substrate for device manufacturing, illumination is often the preferred method for generating holes.

Illumination of a semiconductor with light that has higher photon energy than the bandgap will excite electrons from the valence band to the conduction band of the material. Bandgap energy is typically measured in electron volts (eV), but may also be measured in nanometers since the photon energy for a given wavelength of light is

$$E = \frac{1240}{\lambda},$$

(2.4)

where $E$ is the photon energy in eV and $\lambda$ is the wavelength of light in nanometers. Excitation of electrons by bandgap light creates electron–hole pairs that drift through the SiC substrate. As
shown in Equations 2.1 and 2.3, the holes interact with SiC. The interaction of holes and HF results in removal of SiC at the hole location.

Holes may be generated in SiC by illuminating it with light below about 390 nm. Light below 390 nm has a photon energy of 3.17 eV, which is higher than the bandgap of most common SiC substrates. Figure 2.1 shows that when the wavelength is greater than 390 nm, 4H SiC absorbs very little light [25]. Limited absorption occurs in this band because the photon energy of the light is lower than the band gap energy of the SiC. This means the photons passing through the SiC do not interact with the atoms in the material, so holes are not generated. Light below 390 nanometers has sufficient photon energy to interact with the atoms in the material, and is thus heavily absorbed. This is because the photon energy exceeds the bandgap energy of the SiC, resulting in the photons being consumed in order to promote electrons from the valence band to the conduction band. The bandgap of the SiC substrate changes with the crystal lattice structure, or polytype. Thus, different illumination wavelengths must be used depending on the polytype of the SiC being etched.

![Figure 2.1: A plot of absorption vs wavelength for 4H silicon carbide.](image)

Etching of silicon carbide while illuminated by UV light has many applications if the illumination can be made selective. These applications include pressure sensors [26], piezoresistors [27], porous SiC layers for optical components [28] and many more [29]–[31]. Shor et al. [19] has shown that masking layers can be used to select where the ultraviolet light contacts the SiC material. These masking layers allow the etching of select surface profile features.
Scattered illumination light can effect results during PEC etching processes. When scattered light is absorbed by the SiC substrate, holes are generated and etching occurs. Absorption of scattered light and subsequent etching at regions of the substrate where etching is not desirable can yield structures with high surface roughness and unwanted shapes. The creation of undesired etch features can make machined structures unsuitable for desired applications. Some scattered light will be present when performing PEC etching with bandgap light. Therefore, some undesired etch will be present in the final etched structure, regardless of whether an etch mask was used or not.

### 2.1.2 Two-Photon Absorption

Through the innovative process of coupling two-photon absorption (TPA) with PEC, 3D structures may be machined that no other conventional method or combination of conventional methods can make. TPA is the key to generating holes and subsequent etch features in locations that cannot be etched through traditional wet or dry etching techniques. This technique generates holes in precisely controlled locations, allowing selective etching of the SiC. The presence of holes at these controlled locations allows electrochemical etching to occur. This new method can machine complicated 3D structures beneath the surface of the SiC; something no other method can achieve to date.

Figure 2.2 shows that TPA PEC etching begins with the focus of the laser at the SiC-HF interface. Holes are generated by TPA at the focal point, resulting in etching. The focal point may then be translated into or across the surface to make etched lines and undercuts. Etching will occur wherever holes and HF are both present. Because sub-bandgap light is used, holes are only generated at the focus of the beam where optical intensities are high enough for TPA to occur. This results in localized etching of the SiC substrate and the ability to form undercut features. The use of sub-bandgap light also means that no single photon absorption, or linear absorption, occurs. The lack of linear absorption means that no etching will occur due to scattered light.

Creation of localized concentrations of holes in silicon carbide is critical to development of a single tool etching process. The key to generating localized concentrations of holes in SiC for electrochemical etching purposes is TPA. TPA is a phenomena where two photons excite an electron at the same time resulting in twice the excitation energy. The combined energy of the sub-bandgap photons add to an energy greater than the bandgap of the semiconductor. The combined
energy promotes an electron to the conduction band, forming an electron-hole pair. The hole is then available to react with HF, resulting in PEC etching of the SiC substrate at the hole location.

The rate of light absorption in a material is dependent on the optical intensity of the light. This rate is defined as

$$\frac{-dI}{dz} = \alpha I + \beta I^2,$$  \hspace{1cm} (2.5)

where $dz$ is the thickness of the slice of material, $\alpha$ is the linear absorption coefficient, $\beta$ is the TPA coefficient, and $I$ is the irradiance. Because sub-bandgap light is used for TPA PEC etching, $\alpha$ is zero. This means that absorption in the material is limited to locations where TPA occurs. Therefore, holes will only be generated where TPA occurs.

For PEC etching in SiC to occur, the generated holes must be present at the SiC–HF interface. Some portion of generated holes will recombine in the substrate and others will participate in the PEC reaction to etch SiC. Generation of excess holes in this case is desired because if more holes are generated then more holes are available to react with the HF solution. The excess of holes accelerates the PEC etching reaction. As a rapid removal rate is generally desired, it is beneficial to generate as many holes as possible. To generate a large number of holes, high irradiance, or optical intensity, is required.

The two methods used to attain higher irradiance are focusing the beam to a tight focus and using a femtosecond laser. A tighter focus increases the intensity of the beam at the focus. Figure 2.3 shows that TPA occurs primarily where the light is very tightly focused. The generation of electron-hole pairs is limited to the volume around the focus; thus, only the volume of SiC at
the focus of the beam will be etched. Once the material at the focus of the beam is removed, no carriers are generated and etching stops. Because of this inherent etch stop mechanism, the TPA PEC technique is highly selective.

![Image](https://via.placeholder.com/150)

**Figure 2.3:** (a) When the laser focus is in the SiC, holes are generated through TPA and PEC etching occurs. (b) When the laser focus is no longer in the SiC there is no TPA. Thus, no holes are generated and the PEC etching stops.

Etching by TPA makes etching due to scattered light negligible. Etching due to scattered light is negligible in this case because scattered light has low intensity. Low intensity results in a negligible amount of TPA occurring. Therefore, etching does not occur in locations where scattered sub-bandgap light is incident to the etch surface.

Generation of electron-hole pairs by TPA with sub-bandgap light requires an intense focal point within the substrate. Developments in femtosecond pulsed lasers have made achieving the required intensity easier because the pulse energy is compressed into a very short pulse. The peak power increases linearly with a decrease in pulse duration. This means that shorter pulses have higher power. High peak power over a small focal point results in large optical intensities capable of achieving conditions where TPA may occur.

TPA PEC etching has been demonstrated using our experimental system. Figure 2.4 shows the result of the etching procedure on a 4H n-type SiC wafer with the focal point of the beam at various depths relative to the SiC surface. As the focal point is moved further away from the surface, the beam diameter incident to the wafer surface increases, and thus the intensity of the light on the surface decreases. With this decrease in intensity comes a decrease in hole generation as seen by the more faint etch marks towards the top of the etch depicted in Figure 2.4.
2.2 Surface Detection & Focal Point Placement

The SiC substrate may be etched from the front or back side of the wafer to obtain different types of structures. It is generally advisable to etch surface relief features on the front of the wafer because less light is absorbed through the SiC bulk and thus higher optical intensities are present at the etch interface. Higher optical intensity assists in achieving higher etch rates for 2D surface relief features. However, high aspect and undercut features are difficult to etch from the front of the wafer because previously etched regions scatter light before it comes to a tight focus inside the SiC bulk. Because of this, high aspect and undercut features are generally etched from the back side of the wafer. By etching from the backside, previously etched points do not interfere with etch points deeper into the surface and thus the scattering due to these previously etched points is negligible.

Placement of the laser focus on the surface of the wafer is critical to the etching procedure for both front and back side etching methods. Because holes recombine over a short distance, holes are only present at or near the focus of the laser beam, where they have been generated. This means
that for etching to begin, the focus must be placed precisely on the surface of the SiC substrate. Without proper placement of the focus, TPA and subsequent etching do not occur. Two optical sub-assemblies make placement of the focus on the substrate surface easier.

Two optical tools are employed to ensure that the focus of the beam lies directly on the surface of the substrate being etched. The tools used to detect and place the focal point on the surface are an optical microscope assembly and a confocal detector assembly. Details of these surface detection tools are covered in Chapter 3.
CHAPTER 3. EXPERIMENTAL SETUP

3.1 Etch Chamber and Position Control

The chamber that holds HF solution and the SiC substrate drives many critical requirements of the experimental setup. The materials that the chamber may be fabricated from are limited because of the use of HF in the experiments. The materials that may be used to make the chamber introduce limits on many of the dimensions of the chamber itself. Because the design of the chamber drives the requirements of many optical components within the experimental setup, it is prudent to discuss its design and fabrication prior to a discussion of optical assemblies used in TPA PEC experiments.

3.1.1 Etch Chamber

The experimental chamber in which SiC is etched must be resistant to HF and must allow light to reach the surface of the SiC wafer with fluid reservoirs on each side of the wafer. Figure 3.1 shows the chamber design. The actual chamber has been machined from HDPE with HF resistant Viton O-rings to create fluid seals and sapphire windows, which are both transparent to visible light and resistant to HF. This chamber design is versatile in that it allows HF to be placed in either the front or back fluid reservoirs, allowing the SiC to be etched either from the front or back side. The input and output fluid nozzles also provide the ability to cycle HF through the chamber throughout an etch to maintain fluid temperature or change HF concentration during an experiment.

Safety of the users while handling the etch chamber is important. The addition of inlet and outlet fluid ports to the chamber design shown in Figure 3.2 allow users to pump HF solution into the fluid reservoirs using a peristaltic pump. The use of a pump eliminates many of the risks associated with directly handling the HF solution since it removes the need to pipette HF into the fluid reservoir by hand.
Figure 3.1: The etch chamber used for two-photon assisted electrochemical etching. Chamber sections are machined from HDPE. O-rings are made of chemically resistant Viton. Fluid reservoirs may be filled via HDPE tube fittings.

Figure 3.2: (Left) The etch chamber. (Right) The etch chamber in experimental position.
To etch on the front side of a wafer, HF must be present in the fluid chamber that is positioned between the SiC wafer and the final lens of the optical system. Due to limitations in machining of parts, the minimum fluid chamber thickness achieved in the design is approximately 5.5 millimeters. This measurement establishes the minimum working distance requirement of the objective used in the optical assembly.

3.1.2 Position Control

Fine positioning of the laser focus on the SiC substrate is critical for TPA PEC etching experiments and is necessary for creation of complex structures. Because movement of optical assemblies themselves would cause variations in the optical alignment, the etch chamber should be moved in relation to the beam focus instead. Additionally, because focal points, and thus etch points may be limited to micrometer resolution, the movement platform should have a minimum step resolution of 0.5 μm. These decisions led to the selection of a 3-axis stage with 0.25 μm step resolution in each axis.

The movements of the stage are carried out by stepper motors. Each of the stepper motors has been equipped with rotary encoders for closed-loop feedback. The encoders allow for dynamic control over the positioning of the stage in each axis.

3.2 Optical Assemblies

The optical components, setup, and alignment for the experimental system are crucial for obtaining high quality etch results and rapid etch rates. To achieve the high optical intensity required for TPA to occur, a femtosecond laser and high numerical aperture (NA) objective are used. A long working distance objective is also required due to the minimum working distance specified by the chamber design. A high NA microscope objective is used as the focusing element in the etching setup because a high NA relates to a smaller spot size. A small spot size assists in obtaining high resolution, rapid etching, and high optical intensities. Femtosecond lasers provide the peak optical intensities required for TPA to occur. The focusing objective used in our setup is a Mitutoyo 0.7 NA, 6mm working distance objective. The laser used is a Amplitude Satsuma femtosecond laser.
3.2.1 Main Optical Path

The main optical assembly used for etching SiC is made up of the laser, folding mirrors, and the microscope objective. The folding mirrors and objective may be adjusted for proper alignment with pitch and yaw adjusters on the mirror mounts and XY adjusters on the objective mount. Figure 3.3 shows that the laser beam is directed into a high NA objective lens by folding mirrors. The objective focuses the beam to a near diffraction limited focus. Figure 3.4 shows the expanded optical setup with additional optics used for data collection, feedback, and diagnostic purposes. The expanded optical system may be grouped into subsystems as shown in Figure 3.4. These diagnostic subsystems function as a confocal detector and optical microscope and are essential for etching. Their functions and setup are described below.

Figure 3.3: The simplified optical setup used to etch in SiC using TPA PEC.

Figure 3.5 shows the full experimental setup. Folding mirrors with pitch and yaw adjustment are used to steer the beam. The in-situ microscope and confocal detector assembly are outlined in yellow. The microscope objective is placed on an XY translation mount. All optics are mounted in a 30 mm cage system to help ensure stability and reduce misalignment. The etch chamber is located on a 3-axis stage. The optical assemblies are mounted to a optical breadboard, which is resting on a vibration isolation table, not pictured here. The entire system is enclosed in a fume hood used to vent HF vapor from experiments.
Figure 3.4: The expanded optical setup, with diagnostic sub-assemblies, used to etch in SiC using TPA PEC.

Figure 3.5: The optical setup used for TPA PEC etching. The laser is not pictured, but is located above the setup. A periscope is used to direct the beam down to the height of other optics.
3.2.2 High Numerical Aperture

A high NA objective provides smaller spot sizes and higher peak optical intensities. Laser beams generally have near Gaussian intensity distributions across the beam. Because laser beams have Gaussian intensity distributions, Gaussian beam calculations may be used to calculate the spot size and intensity distributions at a focal point. Using geometrical optics, a high NA relates to a steep focusing angle as given by

\[ \text{NA} = n \sin \theta, \]  

(3.1)

where \( n \) is the index of refraction of the final media in which the beam is focused, and \( \theta \) is the angle from normal at which the beam approaches the focal plane. Using Gaussian beam calculations, a high focusing angle relates to a small beam waist, \( W_0 \), as given by

\[ W_0 = \frac{\lambda}{\pi \theta} \]  

(3.2)

where \( \lambda \) is the wavelength of light being used.

A small beam waist, or spot size, is necessary to achieve good etching results when using TPA PEC etching for two reasons. Firstly, a smaller spot size results in more highly localized hole generation, and therefore, higher resolution etching. This is because holes are only generated at regions of high optical intensity, the optical focus, where TPA occurs. Etching only occurs in the presence of generated holes. Secondly, a smaller spot size results in higher peak optical intensity, which increases the TPA absorption as shown in Equation 2.5. Higher TPA absorption relates to higher hole generation rates.

The beam waist as a function of distance, \( z \), from the focus of a Gaussian beam is described as

\[ W(z) = W_0 \left[ 1 + \left( \frac{z}{z_0} \right)^2 \right]^{\frac{1}{2}} \]  

(3.3)

where \( z_0 \) is the Raleigh range defined by

\[ z_0 = \frac{W_0}{\theta} \]  

(3.4)
The optical intensity profile at some radial distance, $\rho$, and axial distance, $z$, from the focus is

$$I(\rho, z) = \frac{2P}{\pi W^2(z)} \exp \left[ -\frac{2\rho^2}{W^2(z)} \right],$$

(3.5)

where $P$ is the power of the beam.

Figure 3.6 shows the result of applying Equations 3.1 - 3.5 using an NA of 0.7 in air and SiC. The Raleigh range $z_0$ is much shorter for air than for SiC. Likewise, the peak intensity is higher in air where the beam has a smaller Raleigh range. An increase in peak optical intensity relates to increased TPA as shown by Equation 2.5. Increased rates of TPA lead to a more rapid etching rate.

Figure 3.6: (Top-Left) Beam waist, $W_0$, of the incident beam when the beam has passed through air ($n = 1.0$) and SiC ($n = 2.55$). (Top-Right) Irradiance, $I$, versus radial distance, $\rho$, at $z = 0$. (Bottom-Left) Irradiance versus the axial position, $z$, at $\rho = 0$. 

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Figure 3.7 shows the intensity squared cross section of the focused beam in air and SiC, with all other parameters being identical. The intensity is squared in these plots to show the relationship in absorption and subsequent hole generation rate as defined by Equation 2.5. Each of these cross sections is rotationally symmetric about $\rho = 0$. This shows that when a beam with the same NA is focused into a higher refractive index material, the focus stretches in the axial direction, decreasing the axial resolution of the etch region. This creates a stretched etch voxel, or volumetric pixel.

![Figure 3.7: (Top) Gaussian intensity squared profile in air. (Bottom) Gaussian intensity squared profile in SiC.](image1)

Figure 3.8 shows a sketch of a voxel. As the index of material increases, the voxel lengthens, making a larger etch volume. The increase in voxel size is due to the change in beam waist and Raleigh range as shown in Figure 3.6. The increased voxel size results in a larger hole generation volume and thus a larger etched feature. The intensity within the voxels decreases with an increase in beam waist and Raleigh range. This decrease in intensity results in a slower absorption and hole generation rate as shown by Equation 2.5. Therefore, larger voxels have lower etch rate, assuming all other parameters remain constant.
Figure 3.8: A representation of an etch voxel with axial position, $z$, as the major axis and radial position $\rho$ as the minor axis. The origin is marked at the center of the etch voxel.

The change in voxel size for a material is due to refraction of the rays of light when passing through an interface with a change in index of refraction as explained by

$$\frac{\sin \theta_2}{\sin \theta_1} = \frac{n_1}{n_2} \quad (3.6)$$

The reduction in angle caused by refraction when light passes from a low index material into a high index material results in a lower NA in the higher index material. Figure 3.9 shows that if light passes through high index materials then the beam will have a lower effective NA in the higher index material due to a reduction in angle of the incident ray as explained by Equation 3.6. The reduction in NA causes a wider beam waist, longer Raleigh range, and an overall decrease in peak optical intensity as outlined in Equations 3.2-3.5. The increase in beam waist and Raleigh range, coupled with lower optical intensities, results in lower etch resolution and decreased etch rate.

### 3.2.3 Long Working Distance

A long working distance objective is used when large clearances are needed between the final lens of the objective and the focal plane. Because there are limitations to the design and manufacture of the experimental etch chamber, a large clearance gap between the objective lens and focal plane was required. This limitation drove the use of a 6 millimeter working distance objective in our experiments.
Figure 3.9: A demonstration of Snell’s law when a ray passes from air into SiC.

Figure 3.10 shows three different etching methods that may be employed to etch SiC. This figure shows that when the beam passes through media other than air, the effective working distance is increased and the NA is decreased. This is due to refraction through the surface as described by Equation 3.6. In the case of backside etching with a front conducting fluid, the working distance is increased by 1.4 millimeters at the cost of a lower NA, namely an NA of 0.3. Note that Figure 3.10 represents the same objective NA and working distance, and the etch chamber fluid and wafer thicknesses used in our experimental setup.

Figure 3.11a shows a sketch of the etch chamber and objective lens used when performing an etch. The minimum feature sizes of the etch chamber are less than 0.2 mm, indicating that the fluid reservoir sections are near as thin as possible without a major redesign. The objective must be brought within 2 mm of the front sapphire window. The close proximity of the objective and sapphire window results in a high risk of objective damage if the sapphire window was to hit the final lens of the objective during an etching procedure. Figure 3.11b shows this same perspective on the actual hardware components.
Figure 3.10: (Top) Etching on the front side. (Middle) Etching on the backside. (Bottom) Etching on the backside with front fluid.

Figure 3.11: (a) A sketch of the placement of the objective when etching on the backside of SiC with a 0.7 NA, 6 mm working distance objective. (b) The actual placement of the objective and etch chamber when used in TPA PEC etching experiments.
While there are many objectives that have a long working distance, they are generally limited to low NA, a characteristic that is unable to provide the conditions necessary for high resolution TPA PEC etching as discussed in Section 3.2.2. Microscope objectives with high NA and a long working distance are expensive, a factor driven by their strict design requirements. Not only do these objectives correct for many common optical aberrations, as many objectives do, but they must also expand the beam so that a higher NA can be obtained while maintaining a long working distance. A long working distance is required to provide space for fluid sections between the objective lens and the sapphire window that make up the front surface of the etch chamber fluid reservoir.

Figure 3.12 shows a simplified illustration of how a beam must be expanded to achieve a longer working distance while maintaining a high NA. A negative lens is used to expand a small diameter beam to a larger beam. The expanded beam is then focused to a spot by a positive lens. The principal plane marks the location where the final lens of the assembly would be placed to achieve the same NA if the beam was not expanded. The distance from the positive lens to the focal plane defines the total working distance of the objective. The expansion of the beam in the case of Figure 3.12 allows for an almost 2x increase in working distance of the objective while maintaining the same NA.

![Figure 3.12: A simplified design of a high NA, long working distance objective.](image)
Custom optical assemblies utilizing beam expanders, large diameter lenses, and a high power final lens may achieve similar, if not better, working distance and NA as a commercial objective. The drawback to these custom assemblies is that complications occur when designing these systems due to the tight tolerances required for good optical performance. Commercial objectives have been designed by optics experts who have optimized the performance of the objective to correct for a large number of common optical aberrations. Custom design of high NA, long working distance optical assemblies is not recommended due to the limitations in time, budget, and necessary optical alignment equipment to achieve good optical performance. Results of doing so in our research have had limited success. Figure 3.13 shows beam aberrations seen in our experimental system when alignment was incorrect. Both images show a non-Gaussian shape which resulted in etched rings around the intended etch point.

Figure 3.13: (Left) The focus relative to the wafer surface and its optical intensity cross-section when the focus is placed a few µm in front of the wafer surface with a custom optical assembly. (Right) The focus relative to the wafer surface and its relative optical intensity cross-section when the focus is placed a few µm into the wafer surface with the same optical assembly.
Figure 3.14 shows the difference in etch results for single spots when using a custom high NA optical design versus a commercial high NA objective. The etched spots when using a commercial high NA, long working distance objective were much more uniform and demonstrated a higher etch rate.

![Figure 3.14](image)

**Figure 3.14:** (Left) Etch spots resulting from use of a custom optical focusing assembly. (Right) Etch spots resulting from use of a high, 0.7 NA, commercial focusing objective.

### 3.2.4 Confocal Detector Assembly

Confocal microscopes are most often used for imaging samples in which depth information is important. Their construction allows cross-sectional image slices of a sample to be collected by imaging only the parts of the sample that lie in the focal plane. Because the focal plane of an optical system can be limited to hundreds of nanometers in depth, multiple images can be captured at varying depths with high resolution. The resultant images can then be processed to produce high resolution volumetric data for a given sample.

Figure 3.15 shows that a confocal microscope uses a laser that acts as a point source optical beam. The microscope objective focuses the expanding beam onto the sample. A typical confocal microscope uses fluorescence. Light is emitted from the sample location illuminated by the optical source. The back-emitted light is then refocused to a point after reflecting off a dichroic mirror.

The confocal microscope uses a pinhole at the focus of the back-emitted light. Only emitted light from the beam focus will pass through the pinhole. Any light emitted from areas of the sample
outside of the beam focus will not produce a focus at the correct location on the pinhole, resulting in the majority of the out of focus light being blocked. Thus, the confocal microscope only measures the light that is emitted from a small volume near the focus of the laser as defined by the axial and lateral resolution of the system. This allows only the areas of an image within the focal plane to be translated to the image plane, providing a depiction of which features of a sample lie within a given focal plane.

Figure 3.15: Construction of a typical confocal microscope system. Excitation light is focused onto a sample. Any scattered light that lies within the focal plane of the objective is focused through a pinhole and collected by a detector. Scattered light that lies outside of the focal plane is not collected.

Confocal microscopes use a single wavelength excitation source such as a laser to illuminate points on a sample. This collimated excitation light passes through a dichroic mirror that allows excitation light to pass but reflects scattered light emitted from a sample. The excitation light is focused to a point with a microscope objective. Scattered light from the sample is collected by the objective and collimated. The scattered light is then reflected by the dichroic mirror and focused through a pinhole by a focusing lens. The light that passes through the pinhole is collected by a detector. As Figure 3.15 shows, scattered light that remains out of focus is not collected by the pinhole and thus does not become part of the final image. In this way, the intensity of the coupled
scattered light from a single point on a sample may be recorded. By recording the intensity of scattered light at various points on a sample, an image may be constructed.

The design of confocal systems requires that the focused light from the objective probes various locations on a sample if a full image is desired. This is typically achieved through the use of scanning mirrors that scan the beam on the sample, thereby allowing scattered light from various points on the sample to be recorded in a rastered image [32], [33]. Other methods of probing various sample points with confocal systems include the use of microlenses and spinning pinhole disks [34], [35].

Resolution of a confocal microscope system is limited by the NA of the objective and the pinhole size. The lateral resolution of a single wavelength confocal system is limited to

$$R_{xy} = \frac{0.61\lambda}{\text{NA}_{\text{obj}}}$$

(3.7)

where $\text{NA}_{\text{obj}}$ is the numerical aperture of the imaging objective. Axial resolution $\Delta z_{\text{axial}}$ has also been shown to follow

$$\Delta z_{\text{axial}} = \frac{1.5n\lambda}{\text{NA}_{\text{obj}}^2},$$

(3.8)

where $n$ is the index of refraction of the media being imaged and $\lambda$ is the wavelength of the excitation source. Figure 3.16 shows a plot of the axial resolution of a confocal system with respect to numerical aperture of the focusing objective. The pinhole size is matched to the diameter of the focus produced by the confocal focusing lens to achieve the highest possible resolution.

The use of a pinhole prior to the detecting surface provides significant appeal to confocal microscope systems. A pinhole of proper size limits the amount of out-of-focus scattered light incident to the detector surface, thereby causing objects outside of the focal plane to be excluded from a rastered image. This not only allows images of slices of a sample to be captured, but also excludes out of focus features from the image, providing higher image quality than a typical optical microscope. The lateral resolution of the image may be controlled by changing the size of the pinhole. Use of the smallest allowable pinhole defined by the spot size formed by the confocal focusing lens allows less light to reach the detector, forcing longer exposure times but also providing higher resolution images. Photomultiplier tubes are often used as detectors to reduce the
Figure 3.16: Axial resolution ($\Delta z_{\text{axial}}$) as a function of numerical aperture with $\lambda = 550$ nm and $n = 1.5$. Higher NA results in smaller spot size and higher peak optical intensities. The smaller spot size and increase optical intensity drive more rapid and higher resolution etching.

exposure time required for a proper image. Use of larger pinholes reduces the resolution of the resulting image while also minimizing the necessary exposure time.

For use in surface detection where the sample typically contains planar surfaces with very little surface detail, it is only important to know that a face of the sample is located at the focal plane. This means that it is not necessary to scan the focus across the surface as done in standard confocal microscopy. Only a single pixel, or planar location, must be scanned in the axial direction to provide an indication of when the focus has reached the surface. Since confocal microscopes are constructed specifically to give an indication of which features of a sample lie in a focal plane, they are ideally suited for surface detection of planar samples.

In our research it is important that we place the focus of a beam directly on the surface of the media that we are etching. Most often the media that we observe has planar surfaces. The surfaces that we etch are also generally immersed in liquids. This provides several interfaces at which excitation light may be scattered, making it generally difficult to locate the surfaces of the
media with a laser source. By using a modified confocal microscope system, this task is made much easier.

Figure 3.17 shows a modified confocal microscope used in our research. Collimated laser light passes through a beam sampler and is focused onto a surface by a microscope objective. The reflected light is again collimated through the objective and a portion of it is picked off by the beam sampler. The picked off portion is then focused through a pinhole that is located at the focus of the confocal focusing lens. A detector samples the light that has passed through the pinhole. Any light that was not reflected from the microscope objective focus will not refocus to the correct location on the pinhole and will be blocked. This causes most of the out of focus scattered light to be rejected from the detector surface. Light that was scattered from the microscope objective focus will be refocused through the pinhole and onto the detector.

![Diagram of confocal microscope](image)

Figure 3.17: (Top) The focal point is placed directly on the wafer surface. Scattered light is focused through the pinhole, resulting in a high detectable signal. (Bottom) The focal point is not placed directly on the wafer surface. Scattered light is not focused through the pinhole, resulting in low detectable signal.
The use of a pinhole in the confocal system shown in Figure 3.17 allows only scattered light from the volume of the beam focus to be sampled. Scattered light outside of a lateral cross section of the beam focus will not be refocused through the pinhole, but rather to the sides of it. Figure 3.17 shows that scattered light from regions of a surface that do not lie in the focal plane of the focus will be focused either before or after the pinhole and will therefore not pass to the detector. This results in loss of detected signal when the sample does not lie in the focal plane of the microscope objective.

Since only scattered light from the focal plane of the excitation beam will be detected, a higher detected signal suggests that the focus of the beam lies on the surface of the sample. This allows a user to use the laser to locate the surface of any media by observing the detected signal that passes through the pinhole of a confocal system.

Figure 3.18 shows an image of a sampled planar location as the focus is translated through the sample. The resolution of the peaks in Figure 3.18 is defined by the numerical aperture and the confocal pinhole size used in the confocal system setup. A higher numerical aperture yields a smaller spot size. Since scattered light from outside of the spot area will not focus through the pinhole, a smaller spot area yields higher resolution both laterally and axially. This means that the peaks in Figure 3.18 denote that the focal point lies on a surface of the wafer. A higher detectable signal means that the focal point is closer to the wafer surface.

![Figure 3.18](image.png)

*Figure 3.18: A plot of experimental data collected when locating the front and back surfaces of a sapphire window using the confocal detector assembly.*
Figure 3.19 shows the components used in our experimental setup. An Amplitude Satsuma femtosecond laser with a harmonic doubler is used as a 515 nanometer laser excitation source. A Mitutoyo 0.7 NA microscope objective is used to focus the excitation beam. A Thorlabs BSF20-A beam sampler, mounted in a 45° pick-off mount with pitch and yaw adjustment, is used to pick off the confocal sample beam. An Olympus Tokyo 0.25 NA microscope objective is used as the confocal focusing lens. A 20 micrometer pinhole is used. The pinhole is mounted in a XYZ translation mount for precise positioning of the pinhole relative to the focus of the confocal focusing objective. A Thorlabs S120C photodiode power sensor is used as the detector.

Figure 3.19: The confocal detector assembly used in our experiments.
3.2.5 In-situ Optical Microscope Assembly

The addition of an in-situ optical microscope assembly is invaluable in the etching setup. It provides significant data for several crucial elements of the etching process, including alignment, etch progress, etch characterization, and a second check for surface detection. While all of these functions are important, the foremost reason for using the in-situ microscope is alignment of the focusing objective and confocal pinhole.

While the confocal microscope data is essential for discerning etch rates, locating wafer surfaces, and general data acquisition and feedback, the confocal microscope is next to useless if it is not aligned properly. The confocal microscope assembly must be aligned while the focus is resting on the surface of a substrate such as a sapphire window or SiC wafer. Because it is difficult to know if the focus is on the surface without the confocal system being previously aligned, a system must be put in place to give a reliable estimate of focus position. The in-situ microscope is ideally suited for this purpose.

The microscope assembly is made up of a shortpass dichroic mirror, a tube lens, and a CMOS detector. Figure 3.20 shows that the dichroic mirror directs reflected illumination light from the surface of the wafer to a tube lens while passing most of the laser light. The tube lens focuses this reflected light onto a CMOS sensor. The objective lens magnifies the image as seen by the CMOS sensor. Because a 100x magnification objective lens is used, very small details can be seen in the images. This means that the spot incident to the wafer surface can be viewed at a 100x magnification, making it easy to observe aberrations in the spot and correct for them. Uses of this subsystem include alignment of the confocal pinhole, analysis of the laser spot size and quality, and in-situ imaging of the SiC substrate before, during, and after etching.

The in-situ microscope gives feedback on the size of the focus at the focal plane of the microscope objective. Figure 3.21 shows that as the wafer is scanned closer to the focal plane, the spot becomes much smaller, indicating that the wafer is coming closer to the focus of the laser. When the spot has reached its minimum size, the focus of the laser is resting on the surface of the wafer. At this point the confocal system may be aligned. Images obtained by the in-situ microscope allow for a second check in determining if the focus is on the surface of the wafer after the confocal assembly has been aligned. This second check allows viewers to quickly recognize if the confocal system has become detuned over time and to fix the issue promptly.
A high magnification objective is used as the focusing objective for the etching process. The in-situ microscope has the same magnification as the objective itself since the objective is the focusing element. This allows small features to be seen on the surface of the wafer. One of the most important of these features to see is the quality of the laser focus. Uniform and symmetric etch points are desired. This makes removal of aberrations an important factor in achieving a quality etch. If aberrations are present in the beam focus, the spread of energy at the focus will not be rotationally symmetric and non-uniform etch points will be the result. The in-situ microscope
allows viewing of the spot during fine alignment of the objective. This makes it much simpler to fine tune the alignment of the objective to remove aberrations and get a good quality of focus.

The high magnification of the in-situ microscope also allows for qualitative characterization of etched points before, during, and after the etching process. The microscope can easily resolve etched features to give a general sense of whether the etch has succeeded, the shape of the final etched structure, and even the depth of etched points and undercuts. Figure 3.22a shows an image of an etch with an optical microscope focused on the surface of the wafer. Figure 3.22b shows the same image with the microscope focused about 40 \( \mu \text{m} \) below the surface of the wafer, revealing a 40 \( \mu \text{m} \) deep subsurface channel. The in-situ optical microscope can observe these features in the same manner. This means that the in-situ microscope provides almost instant feedback on whether an experiment was successful at both surface relief or subsurface etch processes.

![Figure 3.22: (a) The surface of a SiC after a undercut etch procedure. (b) The undercut as imaged by an optical microscope when focused 40 \( \mu \text{m} \) into the wafer surface.](image)

Fine positioning for machining structures next to or attached to existing structures is necessary for fabrication of complex devices. The in-situ optical microscope allows users to view existing structures and align the starting point of a new etch with previously formed features on a component or device. The same focusing element is used for the etching process and for imaging with the in-situ microscope. This means that there is no deviation from where the focal point is imaged on the wafer and where the etching occurs. This suggests that there is no deviation in po-
sition from the intended etch point and the actual etch point when the etch position is determined through use of the in-situ microscope.

Figure 3.23 shows the in-situ optical microscope in our experimental system. The dichroic mirror is mounted in a 45° pick-off mount with pitch and yaw adjustment. A tube lens is used to focus light onto the CMOS sensor.

![Figure 3.23: The in-situ microscope assembly used in our experiments.](image)

3.3 Laser

Use of a femtosecond laser provides high peak power to achieve high optical intensities at the etch location. The femtosecond laser used in our setup is an Amplitude Satsuma femtosecond
laser with a harmonic doubler module. The harmonic doubler converts the native 1030 nanometer seed laser wavelength to a 515 nanometer output. This 515 nanometer output has an average power of 2.4 watts, a pulse width of 290 femtoseconds, and a pulse energy of 9.6 microjoules. The peak power of the laser may be defined as

\[ P_p = \frac{E_p}{\Delta t}, \]  

(3.9)

where \( P_p \) is the peak power of the laser, \( E_p \) is the energy per pulse, and \( \Delta t \) is the pulse width. This results in a peak power of 33.1 megawatts. Optical intensity, or irradiance, may be defined as

\[ I = \frac{P_p}{A}, \]  

(3.10)

where \( I \) is the irradiance and \( A \) is the area enclosed in the focus of the beam. Using our system specifications we have found that we can obtain optical intensities as high as 2.92\( \times 10^{15} \) watts per square centimeter. Additionally, the fluence \( F \) is defined as

\[ F = \frac{E_p}{A}. \]  

(3.11)

With our system we can achieve fluences of 850 joules per square centimeter.

While obtaining high irradiance will allow for more TPA, and thus faster etch rates as shown in Equation 2.5, high irradiances may also cause damage to optical components and to the SiC substrate itself. Farsari et al. has determined that the ablation threshold of SiC is 0.55 joules per square centimeter when using a 1030 nanometer laser with less than 200 femtosecond pulse [36]. We found that while using our system at 515 nanometer with a 1.5 micron diameter spot size, the ablation threshold was 0.26 joules per square centimeter. This observed decrease in ablation threshold for 515 nanometer light makes sense because SiC absorbs 515 nanometer light more strongly than 1030 nanometer light.

High irradiance may damage optical components used in the optical assemblies, including mirrors, beam samplers, lenses, and other optics. While the laser induced damage thresholds from reputable vendors are often provided, they do not typically have specifications for the threshold when using less than nanosecond pulse widths. It is therefore difficult to determine the damage threshold for our system. To ensure that optical components are not damaged, it is necessary to
keep the beam expanded as it passes through the components. By expanding the beam, the power of the beam is spread over a larger area, which reduces the total fluence.
CHAPTER 4. ETCHING RESULTS

The TPA PEC etching technique has been used to create various test etches without the use of a masking agent. Each etch included in this chapter represents a key result and contribution that allowed further analysis and development of the novel technique used. A more complete selection of less notable etches is included in Appendix C. Etching without TPA using UV light was also tested previously to TPA etching experiments. Results and observations of these experiments are also included.

Metrology of the etched features is required to assess their quality. A brief introduction to metrology techniques for etched features is included. This discussion will aid the reader in understanding the results shown hereafter.

4.1 Metrology

Metrology techniques are crucial for determining whether an etch procedure has worked as intended. Many etch characteristic measurements such as surface roughness, step depth, and edge lengths can be carried out by an optical profilometer. Figure 4.1 shows a profilometer similar to the one used in our research group. Profilometers are often used for semiconductor development to characterize surface topography of lithography features. In the case of TPA PEC etching, a profilometer allows for classical optical imaging, quantification of the roughness of etched features, and the building of a 3D model to quantify etch depth. Figure 4.2 shows a depth profile of an etch cross section as measured by the profilometer. Figure 4.3 shows the profilometer 3D recreation of the etch.
Figure 4.1: A Zeta 3D optical profilometer.

Figure 4.2: (Top) An optical microscope image of several points etched by TPA PEC, taken by the optical profilometer. (Bottom) The depth profile of a cross-section of the etched features.

Figure 4.3: A 3D reconstruction made by the optical profilometer. The etch shown here is the same structure shown in Figure 4.2.
The drawback to using an optical profilometer in the case of SiC etching is that SiC is transparent at visible wavelengths. This makes measurements from an optical profilometer unreliable in cases where polished etching has occurred on SiC. However, TPA PEC etches on SiC to date have exhibited high surface roughness, providing regions where light can reflect back to the profilometer imaging head for accurate depth profile measurements. This allows optical profilometers to be used for imaging and characterizing results obtained from current TPA PEC etching.

Optical profilometers have limited performance when imaging high aspect ratio features. Because of this limitation, other techniques must be used to image high aspect ratio features in SiC. The primary technique used for imaging high aspect ratio features in our research group is use of a scanning electron microscope (SEM) in conjunction with a focused ion beam (FIB) mill.

The SEM shown in Figure 4.4 is capable of obtaining high quality images at magnifications of more than 200,000x. This is very useful when imaging small etch features and etch pits. However, the working principles of the SEM make it incapable of determining the depth of objects. For this reason the FIB is used to mill a stepped cross section into features of interest. Figure 4.5 shows that the milling head is placed at a 52° angle to the SEM head. This allows milling operations to be performed normal to the wafer. The SEM can then be used to image the FIB milled cross section. The imaged features may then be measured with a viewing angle correction to obtain accurate measurements of depth and width of a high aspect feature. This technique may also be used to image cross-sections of subsurface features which are not visible when using an optical profilometer. Figure 4.6 shows an FIB milled etch with angle corrected measurements (denoted ’cs’).

Figure 4.4: The SEM and FIB unit used for SEM imaging and FIB milling procedures used in our research.
Figure 4.5: A diagram of the placement of the sample with respect to the SEM and FIB imaging and milling heads in the SEM unit. These heads are offset by 52° to allow for simultaneous milling and cross-sectional imaging of samples.

Figure 4.6: A sample image taken on the SEM after depositing platinum into a TPA PEC etched pore and subsequent FIB milling operation.
Visual identification of etch features after a milling operation is sometimes difficult. If etch features are filled with other materials, such as platinum, a higher contrast is observed in the collected image, with the SiC being darker and the platinum lighter. The SEM shown in Figure 4.4 can deposit platinum onto a sample. This approach is often used in our imaging steps to make etched features easier to identify. The light coloring of the etched pore in Figure 4.6 is the result of a platinum deposit prior to milling operations.

Imaging of etched SiC features using the SEM in conjunction with the FIB can provide detailed representations of etched features. Three dimensional models of etched features may also be created if a sequence of milling and imaging operations is used to create a z-stack of images. However, the milling operations required to perform this imaging are time intensive. In addition, milling operations are inherently destructive in their nature, making milled structures unusable for their intended applications. Because of this, a different approach to imaging subsurface and 3D structures must be used.

Nondestructive imaging of subsurface features in single crystal SiC is not a heavily researched area because no other technique can make structures that require this imaging. Use of optical microscopes may reveal that subsurface structure exists, but these microscopes are generally unable to provide detailed representations of the 3D feature. The limitations in optical and SEM imaging have driven our research group to explore the use of a confocal fluorescence microscope. The detailed working principle of the general confocal microscope is outlined in Section 3.2.4, but a brief outline of their function will be discussed here.

Confocal fluorescence microscopes provide high axial and planar resolution images by rejecting light from outside the focal plane. Fluorescent dyes used in these microscopes re-emit light of a different wavelength than the excitation light. A filter is used to eliminate collection of excitation light from the final image. This means that confocal fluorescence microscopes only collect light from parts of the focal plane where the fluorescent dye is present. The focal plane of the microscope may be scanned axially through the etch feature to obtain a collection of feature images as a function of axial position. The collection of images may then be stacked in software to create a 3D representation of etched an etched feature. Figure 4.7a shows a single image as taken from the confocal fluorescence microscope. Figure 4.7b shows the 3D representation created from a z-stack of images from the same etch shown in Figure 4.7a.
One challenge that remains when imaging subsurface features with the confocal fluorescence microscope is infiltrating the etch with fluorescent dye. The dyes used are mixed with either water or dimethyl sulfoxide, a low vapor pressure solvent. The mixed dye solution does not readily enter small etched features because the surface of SiC is naturally hydrophobic. The hydrophobic nature of SiC limits the ability of capillary forces to pull the dye solution into subsurface features. To overcome this, our group places a volume of dye over an etch and then places it in a vacuum chamber. Application of vacuum evacuates the air from the subsurface feature. Atmosphere is then reintroduced, allowing atmospheric pressure to force the dye into the subsurface feature. This method has shown mixed results to date. Better solutions to this issue are currently being investigated.

4.2 Etching with UV light

Initial experiments in SiC focused on repeating experiments and results shown by [19] and [20]. These experiments used UV light and single photon absorption to generate holes to participate in the etch reaction. We used the third harmonic tripler module on our laser to achieve a 343 nanometer beam. This corresponds to photon energy of 3.61 eV when using Equation 2.4. The photon energy of 343 nanometer light is above the 3.23 eV band gap of 4H SiC. This means that
each photon in the beam will produce an electron hole to take part in the etching reaction. Because of this, etching will occur at any location where the light is present, including scattered light.

Figure 4.8 shows that etching was achieved where light was incident to the wafer. The grainy surface shows that background etching also occurred because of the presence of scattered light, resulting in porous SiC across the surface. Figure 4.9 shows an SEM image with the beginnings of porous SiC etch pits that covered the entire surface of the wafer at the conclusion of the experiment, showing that etching occurred everywhere that scattered light was present across the surface of the wafer.

Figure 4.8: The result of UV, single photon etching.
4.3 Front-side Etching

There are many benefits to etching silicon carbide from the front, rather than the back. One benefit is that the light does not need to pass through as many material interfaces before it reaches the focal plane, and thus optical aberrations are limited. This makes etching high resolution surface profiles simpler because a small spot, high quality focus, and higher beam intensity, are maintained.

Figure 4.10a shows that when the beam is focused on the front side of the wafer, there is limited optical aberration because the beam does not need to focus through high index materials. The lack of aberrations results in a tight focal point with high optical intensity. The high intensity focus generates a greater number of electron holes which increases the etch rate. Figure 4.10b shows that after the beam has passed through SiC, as it does for back side etching, a high level of optical aberration is observed. The aberrations shown here are spherical aberrations. These aberrations can be explained through application of Equation 3.6 to each incoming ray. The pres-
ence of spherical aberrations stretches the etch voxel and lowers the peak optical intensity of the focus. Thus, for surface relief and low-aspect ratio features, front side etching is preferred due to the limited aberrations encountered.

Figure 4.10: (a) Front side etching results in limited aberration at the focus (b) The focus of the beam demonstrates a high level of aberration when back side etching.

We have demonstrated front-side etching in silicon carbide on many occasions. The features etched from the front-side are limited to surface relief features and low-aspect ratio holes. Each of the front-side etching experiments used 5% HF, 10% ethanol, and 85% deionized water as the etching solution.

Initial experiments etching SiC yielded etch results with very little etch depth due to the inability to position the focus of the beam precisely on the wafer surface, causing low irradiance and etch rate. Figure 4.11 shows an initial front-side etching experiment in SiC where patterns consisted of an L shaped series of dots with a spacing of 10 µm. The focal point was not positioned precisely on the surface of the wafer. Additionally, a commercial focusing objective was not used in the etch setup and therefore too much aberration was present in the focal spot as evidenced by
the Airy pattern at each etch point. The etch points roughened the surface of the wafer but showed little etch depth.

One interesting aspect of the etch shown in Figure 4.11 is that the Airy pattern clearly shows at which locations of the focus the optical intensity was high enough to produce holes through TPA. This proved that etching of SiC through TPA is selective and that etching only occurs where conditions for TPA are met. Additionally, this experiment showed the need to rebuild the optical setup with a higher quality focusing optic to decrease the spot size by decreasing the aberrations. This experiment also indicated that higher resolution surface detection was required to get good results. The methods to achieve a higher resolution surface detection are using a smaller confocal microscope pinhole and more precise optical alignment.

Figure 4.11: (Left) Several arrays of TPA PEC etched points. (Right) A single series of TPA PEC etched points. The points exhibit etching at the optically intense peaks of an Airy pattern.

Figure 4.12 shows the etching of individual points after changing from a custom optical focusing assembly to a commercial 0.7 NA microscope objective yielding much higher quality etch points. The depth of these etched points is about 0.75 μm. This experiment also demonstrated the need for more accurate positioning control because the distance between the various holes was supposed to be the same.
Figure 4.12: (Left) A series of high resolution etched holes. Each hole is about 3.5 µm in diameter. (Right) A depth profile of the etch taken with the profilometer. Each point is measured to be about 0.75 µm deep.

Figure 4.13 shows an array of etched holes. Each 3x3 array of points in Figure 4.13 was etched with the focus at a different axial position, Z, relative to where the focus was measured to be on the surface of the wafer. A negative Z position denotes that the focus is within the wafer while a positive Z position denotes that the focus lies outside the surface of the wafer.

Each of the three horizontal spots in each 3x3 array used the same etching conditions. The characteristics of each of the identical etch spots are very similar demonstrating the consistency of the system. Between each of the three rows a different bias voltage was applied across the wafer to observe the effect a bias voltage would have on the etching. As the bias voltage increases, the resultant electric field pushes holes away from the HF. There is very little change in the shape of the etch with changing bias voltage for the voltages used in this experiment. Thus, the bias voltage is not needed for the SiC etching.

When the focus lies within the wafer, small amounts of etching are observed. Etching occurs when the focus is within the SiC bulk for two reasons. First, the etch voxel is long, meaning holes are still generated at the surface in small amounts even when the main portion of the focus lies within the substrate. Second, the holes drift within the material, allowing some portion of them to reach the etch interface despite the focus not being on the surface. When the focus is off the surface and out of the SiC bulk, much less etching is observed. This is because holes are only generated in the material at a small, low intensity region of the etch voxel.
Larger etch regions may be observed when the focus is slightly within or off the surface of the SiC. This is due to the spot size increasing relative to the surface while still having sufficient optical intensity for TPA and subsequent etching to occur. These larger etch points from off-surface focal points have demonstrated less etch depth than etch points resulting from a focus that lies precisely on the surface of the wafer.

Figure 4.14 shows the set of etch points from Figure 4.13 labeled as $Z = 2$ (the middle right set). In addition to showing the microscope image of these holes, the optical profilometer was used to obtain an estimate of the size and depths of the holes. The resulting measurement shows that the holes have a depth of about $2 \mu m$ with a diameter of about $5 \mu m$.

The FIB was used to more accurately measure of the depths of the holes. Figure 4.15 shows the set of points from Figure 4.13 labeled $Z = 4$. The holes are consistently shaped at each point.
Figure 4.14: A single array of etched pores.

in the array, showing that the etch rate and stage movements are consistent for each etched hole. Note that the bottom-middle hole was milled too far with the FIB, which is why it does not look consistent with the other pores. The etched holes start with a wide opening and taper to a point.

Figure 4.15: A 3x3 array of front–side etched pores. Each hole is near identical to the others, showing consistency in etch rate and stage movement.
Figure 4.16 shows a zoomed in view of the top left hole shown in Figure 4.15. The square hole is the area removed by the FIB to get access to the etched hole. The light gray material is the platinum material deposited into etched hole. Figure 4.16 shows that the pores are 12 µm deep and have a maximum diameter of 5.67 µm and a minimum diameter of 1.48 µm. These holes should have a depth that is close to the optical profilometer measurement shown in Figure 4.14. This shows that the optical profilometer is limited in its ability to accurately measure the depth of high aspect ratio holes.

**Figure 4.16: A single cross sectioned pore as shown in Figure 4.15. A FIB milling cross section was used to expose the pore for imaging by the SEM.**

The etched pores shown in Figure 4.15 were etched without the use of a masking agent. This proves that the TPA PEC etching technique is a direct-write etching technique that can be utilized for surface relief prototyping applications. The pores also show that as the etch deepens,
the pore narrows. This means that etching slows due to limited TPA because the optical intensity at the focus drops due to the beam scattering off previously etched locations.

Figure 4.17 shows that a square was etched, with defined etch points and a blown out corner. The defined etch points in Figure 4.18 show that etching occurs primarily at the center of the focus. The etch points are 3.5 $\mu$m in diameter. Figure 4.18 also shows that the trough bottom is very smooth, with small amounts of surface roughness. The blown out edge was undesired and the cause of it is presently undetermined, but was likely due to a light scattering effect.

Figure 4.19 shows that the sidewalls of the etch are steep and that the maximum depth of the etch was about 2.5 $\mu$m. Figure 4.19 also shows that the area at the center of the etch point is about 0.5 $\mu$m deeper than the surrounding etch area. This demonstrates that more rapid etching occurs at the center of the optical focus where optical intensity is greater.

### 4.4 Back-side Etching

Back-side etching has many advantages over front-side etching when high aspect ratio or 3D features are required.

Figure 4.20a shows that it is more difficult to etch deep features from the front because light is scattered from previously etched locations on the surface, and thus the beam intensity and
Figure 4.18: (Left) An optical microscope image of individual defined etch points from the top line of the etch in Figure 4.17. (Right) A zoomed in SEM image of the individual etch pores.

Figure 4.19: (Top) The depth profile of the top line of the etch in Figure 4.17. (Bottom) A profilometer 3D reconstruction of the etched region.

quality diminishes as the etch progresses deeper into the substrate. This makes etching 3D and subsurface features from the front a difficult task.

When light passes through a rough interface, the light scatters and refracts, resulting in a spread of the beam. Figure 4.20a shows that with front-side etching, the scattering points occur before the focus of the beam resulting in a spread of the beam focus. The spread in the beam focus results in a larger focal spot and less irradiance at the focus. Figure 4.20b illustrates that with
Figure 4.20: (a) With front-side etching the light hits previously etched features causing scattering and refraction before the focus, which causes aberrations in the focus resulting in a larger focal spot. (b) With back-side etching the scattering and refraction occur after the focus, resulting in a tight focal spot.

back-side etching the scattering points occur after the beam focus. This means that when etching from the back-side, the beam focus is not affected by etched locations, resulting in a small spot size and high irradiance.

The decrease in the peak irradiance during front-side etching leads to a reduction in TPA and can result in halted etching because of insufficient hole generation. As the aspect ratio of front-side etched holes increases, the effect of scattering on the spot size increases. Because this effect does not occur when etching from the back-side, back-side etching is needed for undercuts, tubes, and high aspect ratio features.

4.4.1 Surface Relief

The back-side etching technique requires the beam to pass through an additional layer of material, the SiC substrate itself. This causes aberrations in the beam to be more significant than those encountered in the front-side etching method. These additional aberrations are especially significant because of the high optical index of SiC, which is about 2.5 depending on the crystalline structure of the substrate used. Increase in optical aberrations can cause lower etch rates and a
decrease in etch resolution than seen in front-side etching due to the inability to obtain as tight of a focus.

Figure 4.21 shows a simple line of holes etched in the back-side of a wafer. The points have a diameter of 2.4 μm and an average depth of 0.5 μm. However, this depth measurement was made using the optical profilometer. So, the depth might be deeper than 0.5 μm. These holes represent the first backside etching of SiC using TPA PEC.

Figure 4.21: (Left) A series of back-side etched points. (Right) The depth profile of the etched points.

Figure 4.21 also shows that the movements of the 3-axis stage were inconsistent during the experiment. Each etch point should have been equally spaced. These inconsistencies spurred the retrofitting of the 3-axis stage with higher resolution stepper motors and rotary encoders for closed-loop feedback. The retrofitting of the 3-axis stage provided much more consistent movements on subsequent etches, as well as the ability to dynamically correct incorrect movements due to the feedback provided by the rotary encoders.

Figure 4.22 shows a surface relief backside etch of Greg Nielsen’s face. The etch file was generated by the 'image to etch file' script shown in Appendix B. During the course of the etch, the HF fluid leaked below the level of the etch, resulting in only half the structure being noticeably etched. However, small amounts of etching on the right half of the etch may still be observed, likely due to small amounts of residual HF solution on the substrate surface. This etch demonstrates the ability to make arbitrarily shaped surface relief structures using back-side TPA PEC.
4.4.2 Non Line-of-Sight and 3D

An undercut and high aspect hole was formed using the back-side etching technique. Figure 4.23 shows an SEM image of the hole. A FIB was used to cut away the SiC until the hole was cut in half. Figure 4.23 shows that the hole begins at the surface and curves downward into the silicon carbide bulk. Figure 4.24 shows that the feature was formed by focusing first on the back-side of the wafer, then translating the focus into and across the surface as the etch progressed, forming a curve and undercut.

This structure cannot be fabricated using traditional wet or dry etching techniques in SiC. Traditional techniques cannot produce this structure for two reasons. First, traditional techniques have an inherent inability to make undercuts due to their required line-of-sight nature. Second, traditional methods are limited in the aspect ratio that can be produced.

The ability to etch the feature shown in Figure 4.23 proves that arbitrary subsurface shapes may be machined in SiC using our experimental etching technique. Additionally, the presence of solid SiC directly above the bottom of the hole shows that more complex undercuts may be formed.
Figure 4.23: An SEM image of a back-side etched hole with a curve. The deepest section of the hole has solid SiC above it, showing that undercuts are possible. The light grey areas at the entrance and the edges of the hole are redeposited silicon carbide from the focused ion beam milling process.

Figure 4.24: The direction that the focus of the laser was moved to etch a curved and undercut hole in SiC.

using this method. The hole has been measured using the SEM in combination with the FIB to be 27 µm deep and 3.2 µm in diameter.

A surface-parallel hole was etched to demonstrate the ability to etch high aspect features. Figure 4.25 shows the result of the etch. The C-shaped feature on the left of the image was etched to help locate the etch in the microscope. The high-aspect hole itself goes straight into the surface for 20 µm, then parallel to the surface for 230 µm.
Figure 4.25a shows a microscope image of the undercut. The visible line is the roughed up surface over the tube. Figure 4.25b shows an SEM image of the same structure after the FIB was used to expose the far end of the tube. Notice that the roughed up surface over the tube has very little depth. Figure 4.25c is an SEM image of the end of the tube that was exposed by the FIB. Figure 4.25d is a zoomed in SEM image of the hole, which shows that the major axis of the hole at the end is 4.84 $\mu$m and the minor axis is 2.45 $\mu$m, demonstrating an aspect ratio of roughly 80. This feature cannot be created using traditional SiC etching or milling techniques due to the undercut feature.

**Figure 4.25:** (a) An optical microscope image of the surface parallel hole. (b) An SEM image of the surface parallel hole. The right end of the hole shows the result of a FIB milling cross-section. (c) An SEM image of the end undercut hole with solid SiC above after a FIB milling operation. (d) A magnified SEM image of the cross-sectioned hole.
Three U-shaped undercut channels were etched to demonstrate the ability to go down into the SiC substrate and then back to the surface. Figure 4.26 shows a sketch of the feature with lines indicating where cross-sectional images were taken with the combined FIB + SEM. Each of the cross-sections is separated by 2 µm.

![Figure 4.26: A sketch of the U-channel shape with cross-sections labeled. The red area denotes the area milled by the FIB.](image)

Figure 4.27 shows an SEM image of the finished etch, with the three U-channels. There is a small amount of surface etching. The surface etching suggests that there is a small amount of holes present at the surface, while the majority of the holes remain subsurface near the etched channel during the etch. Additionally, each channel is uniform compared to the others with the exception of the bottom-left hole. The bottom-left hole curves down into the bulk of the SiC due to errors in 3-axis stage movements. A low depth, vertical line was etched between the inlet and outlet holes of each channel to make locating the etch location easier on the profilometer and SEM.
Figure 4.27: An SEM image of a series of undercut channels etched in SiC.

Figure 4.28 shows several cross sections of the bottom U-channel in the etch. The undercut was 39.21 µm deep at its deepest point and 4 µm in diameter. The light gray in the Figure 4.28 is redeposited SiC material from the FIB milling operation. Notice that the hole is more circular than the hole in Figure 4.25.

This etch represents the first fully undercut tube with inlet and outlet ports in SiC using a single tool or step to date. Demonstration of the ability to create this structure is the foundation for machining long tubes in single crystal SiC for heat exchanger applications. This etch also shows
Figure 4.28: (a) The exit pore of the undercut channel. (b) The exit pore of the channel with the undercut surface-parallel tube revealed. (c) Only the undercut surface-parallel tube remains. This proves a continuous subsurface channel with entrance and exit holes.

that arbitrary 3D structures may be formed under the surface of the wafer. The major axis of the undercut tube is 8.25 $\mu$m and the minor axis is 4.65 $\mu$m.
CHAPTER 5. SUMMARY

Through the innovative process of coupling two-photon absorption (TPA) with photoelectrochemical etching (PEC), I have demonstrated the fabrication of 3D structures in single crystal SiC. TPA is the key to generating holes and subsequent etch features in locations that cannot be etched through traditional wet or dry etching techniques. This technique generates holes in precisely controlled locations, allowing selective etching of the SiC. The presence of holes at these controlled locations allows electrochemical etching to occur.

Chapter 3 discusses the construction of the system used to create the structures in SiC. My contributions related to the system are the following.

• Selected, assembled, and aligned all optical components for 3D PEC etching in SiC.

• Designed, constructed, and aligned a single pixel confocal microscope system for surface detection of SiC substrates.

• Implemented an in-situ optical microscope for surface detection and imaging of etched substrates.

• Retrofitted a 3-axis stage with stepper motors and drivers with encoder feedback to ensure proper movement in each stage axis.

• Developed a surface transform script for making axial adjustments in wafer position to account for variations in surface position due to motor cross-talk and substrate pitch and yaw.

• Developed and modeled a chamber design to hold the sample wafer in an HF bath with increased user safety, electrolyte cycling, and use of a high numerical aperture objective.

Chapter 4 shows the key structures that were created in SiC and the metrology methods developed to characterize the structures. My contributions related to these areas are the following.
• Developed procedures for imaging of subsurface 3D structures in SiC, including FIB and SEM imaging, optical microscope imaging techniques, and confocal fluorescence microscopy techniques.

• Carried out experimental design for characterization of etch parameters including dwell time, bias voltage and HF concentration for 3D PEC etching.

• Demonstrated surface relief structures in SiC using front-side PEC etching.

• Demonstrated surface relief structures in SiC using back-side PEC etching.

• Demonstrated the fabrication of a tube through SiC. This structure demonstrates the ability of fabricating non-line-of-sight structures in SiC using back-side PEC.

5.1 Future Work

There is much future work that could be accomplished to increase the quality and usefulness of the TPA PEC etching technique. The following paragraphs give a brief description of what future work could entail.

Multi Beam Processing

To date, the etch rate of SiC using TPA PEC etching has been slow. Creation of multiple focal points at the same focal plane would allow for faster etching of parallel undercut tubes, lines, and more. Individual control of the multiple beams in the planar axes would also allow for complex 3D structures to be etched at a much faster rate. This work may include use of diffraction gratings, spatial modulators, acousto-optic modulators, and more.

Heat Exchanger

Creation of complex heat exchangers in single crystal SiC would be a large step forward for the TPA PEC etching technique. SiC has a higher thermal conductivity than most metals, and therefore could hold a unique position in heat exchanger research and development. The ability to create high density and high aspect ratio tubes through the material in arbitrary shapes would prove beneficial for heat exchanger technology. The development of this technology would require faster etch rates to be useful for industrial applications.
REFERENCES


APPENDIX A. OPTICAL ALIGNMENT TOOLS AND PROCEDURES

A.1 Optical Alignment Tools

There are a variety of optical alignment tools available to make alignment procedures much simpler. These tools include adjustable irises, cage mountable alignment targets, shear plates, IR detection cards, and many others. Adjustable irises and cage mountable alignment targets are the main tools used in alignment of the SiC optical setup. Figure A.1 shows these tools.

Figure A.1: Some common optical alignment tools.

A.2 Alignment Procedures

The following alignment procedures should be performed in the order presented. These alignment procedures are subject to change as more subsystem diagnostics are added to the optical assembly. Slight variations of these procedures may be required as system requirements change, but the basic procedure and practices should remain similar.
A.2.1 Folding Mirror Alignment

The first things to be aligned in an optical system are any components that make up the main beam path. In that case of the SiC system, these components include the folding mirrors, dichroic mirror for the in-situ microscope, and beam sampler for the confocal system. The goal is to have the beam pass through the final optical leg with minimal pitch and yaw in relation to the optical axes of the last pointing mirror and final optic, in this case the objective.

To achieve the minimal pitch and yaw of the beam through the final optical leg, a series of pointing and centering mirrors must be used. The two mirrors should be at 90° angles to each other to maximize the available aperture of the mirrors. The first mirror in this series is used to point the beam to the center of the second mirror. The second mirror is then used to center the beam down the optical axis of the final optical leg.

A adjustable iris or cage mountable alignment target is invaluable in the alignment of the folding mirrors. These tools give a clear indication of whether the beam is passing through the optical axis of the system or not. The use of these tools and concurrent alignment of the pointing and centering mirrors may be broken down into the following steps.

1. Place the alignment tool to the location directly before the second mirror, along the optical axis.

2. Adjust the pitch and yaw of the first mirror until the beam passes through the aperture of the alignment tool.

3. Move the alignment tool directly after the second mirror, along the optical axis.

4. Adjust the pitch and yaw of the first mirror until the beam passes through the aperture of the alignment tool.

5. Move the alignment tool away from the second mirror towards the final optic, along the optical axis.

6. Adjust the pitch and yaw of the second mirror until the beam passes through the aperture of the alignment tool.
7. Repeat steps 5-6 until the alignment tool is directly before the final optic and the beam passes through the alignment tool.

**Note:** If the second mirror does not have enough pitch and yaw adjustment, the pitch and yaw of the first mirror may need to be adjusted. This process is a repetitive one. If you can get the alignment close on a first run through the steps, repeat the entire process to get an even better alignment. The goal is for the beam to pass through the center aperture of the aperture of the alignment tool at every position along the final optical leg.

**Note:** Do not under any circumstances adjust the alignment of the folding mirrors for purposes of aligning other subsystems. Doing so will change the alignment for every other subsystem, ruin alignment of the objective lens, and force a full system realignment process.

### A.2.2 In-situ Microscope Alignment

The alignment of the in-situ microscope is not particularly sensitive. Before attempting the following alignment steps, ensure that a high enough neutral density (ND) filter is placed on the front of the detector lens tube to avoid damaging the sensor with the laser. If in doubt, begin with a high ND (5-6) and work to a lower ND until there is a detectable signal on the detector.

These steps assume that the dichroic mirror has already been correctly placed at a near $45^\circ$ angle to the final optical leg during alignment of the folding mirrors and that the objective has been roughly aligned.

1. Determine where the tube lens will be placed. From this location, measure 148 mm (the working distance of the tube lens) back along the optical axis of the tube lens.

2. Place an alignment marker (business card) at the measured location.

3. Put on your laser eye wear.

4. Turn on the laser.

5. Place a mirrored surface (silicon wafer, mirror, etc...) at the focus of the objective.

6. Make a mark on the alignment marker from step 2 where the laser is hitting the card.
7. Place the tube lens in the desired location.

8. Adjust the position of tube lens until the focus of the beam is hitting the card in the same marked location from step 6.

9. Remove the alignment card and insert the image detector at the location where the card was.

10. Adjust the position of the image detector until the reflected spot from the laser appears in the center of the image detector.

A.2.3 Confocal Microscope Alignment

The alignment of the confocal microscope system is critical to detecting the surface of the SiC wafer and good etching results. The steps outlined here assume that the folding mirror alignment, rough objective alignment, in-situ microscope alignment have all been performed with the beam splitter installed at a 45° angle to the final optical leg during folding mirror alignment.

1. Place a polished silicon wafer at the focus of the objective. The correct placement of the wafer can be determined through use of the microscope system. If the laser appears to be ablating/etching the surface of the wafer, turn down the laser power and move to a new location on the wafer.

2. Roughly align the confocal focusing lens of objective with the reflected beam from the beam splitter. The beam may not be visible on a card, but the focus should be.

3. Roughly align the pinhole (in an XYZ translation mount) with the focus of the beam.

4. Using the detector software for feedback, adjust the pinhole in the x and y axes until a detectable signal is seen on the detector software. This may take quite a bit of time depending on the size of the pinhole and the quality of the rough alignment.

5. Once a detectable signal is seen, make further adjustments in x and y axes until the detected signal is at its maximum.

6. Adjust the z axis until the detectable signal is at its maximum.
7. Repeat steps 5-6 until the detectable signal is at its absolute maximum.

**Note:** This alignment procedure can be extremely time consuming. Plan on at least 2 hours to get the pinhole aligned for maximum detectable signal. This process is also extremely repetitive in terms of adjustments to the translation axes. Take the time necessary to get a quality alignment or you will likely get poor performance from this system.
APPENDIX B. PYTHON CODE

B.1 2D Image to Etch File Script

```python
import matplotlib.pyplot as plt
import numpy as np
from PIL import Image

image = np.array(Image.open('Input_image_name.jpg'))

# Use this command if the image is not grayscale
image = image[:,:,1]

# Specify distance between each pixel (etch point) and the dwell time
scale = 4.
dwell_time = 3.

# Get the image shape
# h : height
# Measured in pixels downward from top left origin of (0,0)
# w : width
# Measured in pixels rightward from top left origin of (0,0)
h = image.shape[0]
w = image.shape[1]

# Convert the image into a boolean representation instead of (0 || 260)
image = np.where(image >= 200, True, False)

# Sanity check
plt.imshow(image)
plt.show()
```
plt.show()

# Save every x,y pixel where there is something to be etched
positions = []
for x in range(w):
    for y in range(h):
        if image[y,x] == False: # This may be changed to True if you want an inverted image
            positions.append([y,x])

# The first move will be to the first pixel to be etched
y_moves = np.array([positions[0][0]])
x_moves = np.array([positions[0][1]])

# Each subsequent move will be relative to the pixel before it
for i in range(1, len(positions)):
    y_moves = np.append(y_moves, [positions[i][0] - positions[i-1][0]])
    x_moves = np.append(x_moves, [positions[i][1] - positions[i-1][1]])

# Format the data
# Etch file format : step_number, x, y, z, unused, dwell, voltage
step_number = np.arange(1,x_moves.size+1,1)
z_moves = np.zeros(x_moves.size)
col4 = np.zeros(x_moves.size)
dwell = np.ones(x_moves.size)*dwell_time
voltage = np.zeros(x_moves.size)

y_moves = y_moves*scale
x_moves = x_moves*scale

out = np.vstack((step_number,z_moves,x_moves,y_moves,col4,dwell,voltage))
out = out.T

np.savetxt('output.csv',out,delimiter=',')
B.2 2D Polynomial Fitting for Transform

```python
import numpy as np
from mpl_toolkits.mplot3d import Axes3D
import matplotlib.pyplot as plt
import sys
from matplotlib import cm
from scipy import interpolate

def polyfit2d(x, y, z, kx=3, ky=3, order=None):
    
    # Two dimensional polynomial fitting by least squares.
    # Fits the functional form f(x,y) = z.

    Notes
    ------
    Resultant fit can be plotted with:
    np.polynomial.polynomial.polygrid2d(x, y, soln.reshape((kx+1, ky+1)))

    Parameters
    ----------
    x, y: array-like, 1d
        x and y coordinates.
    z: np.ndarray, 2d
        Surface to fit.
    kx, ky: int, default is 3
        Polynomial order in x and y, respectively.
    order: int or None, default is None
        If None, all coefficients up to maximum kx, ky, ie. up to and including x^kx*y^ky, are considered.
        If int, coefficients up to a maximum of kx+ky <= order are considered.

    Returns
    -------
    Return parameters from np.linalg.lstsq.
```
soln: np.ndarray
    Array of polynomial coefficients.
residuals: np.ndarray
rank: int
s: np.ndarray

# grid coords
# x, y = np.meshgrid(x, y)
# coefficient array, up to x^kx, y^ky
coeffs = np.ones((kx+1, ky+1))

# solve array
a = np.zeros((coeffs.size, x.size))

# for each coefficient produce array x^i, y^j
for index, (j, i) in enumerate(np.ndindex(coeffs.shape)):
    # do not include powers greater than order
    if order is not None and i + j > order:
        arr = np.zeros_like(x)
    else:
        arr = coeffs[j, i] * x**i * y**j
    a[index] = arr.ravel()

# do leastsq fitting and return leastsq result
return np.linalg.lstsq(a.T, np.ravel(z), rcond=None)


def GetTransformParams(input_file_name, max_ord, plot_flag):
    
    Parameters
    ----------
    input_file_name : string
Name of .csv file containing x,y,z data collected from transform software

max_ord : int
    Max order of fit to calculate

plot_flag : boolean
    TRUE: plots all of the fitted surfaces
    FALSE: omits plotting of the fitted surfaces

Returns
-------

best_coeffs: the best coefficients corresponding to best polynomial fit of the surface

max_r2: the best R squared value from any of the calculated fits

(order_x,order_y): the best order found in the x and y dimensions

Usage
-----

coef,r2,orders = GetTransformParams('points_49_data_set_2_redo.csv',5,True)

x_to_find = 1 (in steps)
y_to_find = 3 (in steps)

eval_point = np.polynomial.polynomial.polyval2d(x_to_find, y_to_find, coeffs)

input_file = open(input_file_name)

# get the data from the input file
data = np.genfromtxt(input_file, delimiter=',', skip_header=0)

# number of sample points in each dimension - assuming a square grid
seps = int(np.sqrt(len(data[:,1])))
# making an assumption that these axes are labeled correctly. Make sure the axes match with the format in which data points were collected.

```python
x_data = data[:,0]
y_data = data[:,1]
z_data = data[:,2]
```

# Because this is the grid that the points were gathered on
```python
xlin = np.linspace(min(x_data),max(x_data),seps)
ylin = np.linspace(min(y_data),max(y_data),seps)
X_data, Y_data = np.meshgrid(xlin,ylin)
Z_data = z_data.reshape((seps,seps))
```

```python
max_order = max_ord+1
r2_vals = np.zeros((max_order,max_order))
max_r2 = 0.
for kx in range(1,max_order):
    for ky in range(1,max_order):
        order = None
        # print(kx,ky)

        # solve for the coefficients with original data format
        soln = polyfit2d(x_data,y_data,z_data,kx,ky,order)
        coeffs = soln[0].reshape((kx+1,ky+1))

        # calculate fitted surface points on grid spacing from experiment
        fitted_surf = np.polynomial.polynomial.polyval2d(X_data,
               Y_data, coeffs )
        try:
            z_fit = fitted_surf.reshape((seps,seps)) # reshape to match 11x11 meshgrid
        except:
            print('Go to .csv and make sure the last row isnt formatted incorrectly')
```

# Normalize to [0,1] to get surface coloring correct
norm = plt.Normalize(z_fit.min(), z_fit.max())

colors = cm.viridis(norm(z_fit))
rcount, ccount, _ = colors.shape

if plot_flag == True:
    # Plotting Stuff
    fig3 = plt.figure()
    ax = fig3.add_subplot(111, projection='3d')

    # Scatter plot the measured points
    plot_meas = ax.scatter(X_data, Y_data, Z_data, cmap='coolwarm')

    # Surface plot the fitted points
    plot_fit = ax.plot_surface(X_data, Y_data, z_fit, rcount=rcount, ccount=ccount, facecolors=colors, shade=False)
    plot_fit.set_facecolor((0,0,0,0))
    ax.set_xlabel('X')
    ax.set_ylabel('Y')
    ax.set_zlabel('Z')

    z_data = np.reshape(z_data,(-1,1))
    z_fit_rs = np.reshape(z_fit,(-1,1))
    Zres = sum((z_data-z_fit_rs)**2)
    Ztot = sum((z_data-z_data.mean())**2)
    r2 = 1.0-(Zres/Ztot)
    r2_vals[kx,ky] = r2
    # print(r2)
    if r2 > max_r2:
        max_r2 = r2
        best_coeffs = coeff
        order_x = kx
        order_y = ky

    return best_coeffs, max_r2, (order_x, order_y)
coef, r2, orders = GetTransformParams('points_49_data_set_2.csv', 4, True)

# Usage to calculate how far in z to move at position (x, y)
x_to_find = 1
y_to_find = 3
eval_point = np.polynomial.polynomial.polyval2d(x_to_find, y_to_find, coef)

# To calculate the z adjustment for a given position
x_to_find = 1  # A randomly x value inside the field of sampled/fitted points
y_to_find = 3  # A randomly y value inside the field of sampled/fitted points
eval_point = np.polynomial.polynomial.polyval2d(x_to_find, y_to_find, coeffs)
ax.scatter(x_to_find, y_to_find, eval_point)
plt.show()
APPENDIX C. EXTENDED ETCHING RESULTS

C.1 Front Side

Images of an L shaped etch that was made with a L shaped line of points. The etched lines are wide, about 40 µm, indicating poor focal point placement on the surface. The etch points on the upper edge of the L are easily identifiable. The top region shows a partially etched region. A longer dwell time would be required to fully etch this region.

Figure C.1: (Left) An optical microscope image of an L shaped etch. (Right) An SEM image of the L shaped etch.
Images of a series of etched lines. At the bottom of the etch, the focal point was placed directly on the surface of the wafer. As the etch progressed upwards, the focal point was moved further away from the wafer surface. This resulted in a decreased amount of etching due to lack of optical intensity and hole generation where the light was incident to the surface. Additionally, greater amounts of etching near bottom portion of each etched point indicate that aberrations were present in the beam, which could be remedied through tuning of the optical alignment. The SEM image shows that individual etch points are easily identifiable by their smooth and round profile. Small amounts of etching occur outside of the main etch point, indicating lesser amounts of TPA in those regions.

Figure C.2: (Left) An optical microscope image of a series of etched lines. (Right) An SEM image of the four lowest lines in the etch.
An optical microscope image of a series of etched lines. The focal point was placed in front of the wafer on the left edge of the etch. The focal point was incrementally moved until it rested on the surface at the middle of the etch. The focal point was further moved into the bulk of the wafer as the etch progressed to the right. The dwell time of each point was varied for each row of etching. Shorter dwell times resulted in less etching in the top row, followed by increased etching in lower etched rows. This helps show the change in etch rate both as the dwell time is changed and as the size of the focal point changes relative to the surface of the wafer.

Figure C.3: An optical microscope image of a series of etched lines.
An optical microscope image of a Panasonic logo etched previous to a presentation to the company. The etch file was generated with the image to etch script as shown in B. Each point was etched with a dwell time of 3 seconds. Little depth is observed at each etch point, but the etched points seen are indicative of small amounts of surface roughness. Time from etch file creation to finished etch was approximately 72 hours, showing the advantage of single tool direct write etching.

Figure C.4: An optical microscope image of an etched Panasonic logo.
C.2 Back Side

An optical microscope image of a cougar shaped surface relief pattern etched on the back side of a SiC wafer. Dwell time for each point was 4 seconds. The etch file was generated using the image to etch script as shown in B. This etch shows the ability to etch arbitrary surface relief shapes on the back side of a wafer. Additionally, the consistency of the etched points indicate that the focal point was very close to the surface throughout the span of the etch. Total time of etch, including creation of the etch file was approximately 60 hours.

![Image of a cougar shaped surface relief pattern etched on the back side of a SiC wafer.](image)

Figure C.5: An optical microscope image of a cougar shaped surface relief pattern etched on the back side of a SiC wafer.
An optical microscope image showing an attempt at an undercut expansion nozzle that could be used for semiconductor chip cooling. The left edge of the hourglass shape is undercut until the middle of the etch where suddenly etching begins at the surface without a change in the axial positioning of the wafer. This likely indicates that the HF solution was depleted at the etch site, resulting in a drop in etch rate. Longer dwell times would allow for more complete diffusion of HF solution to the etch site. A movement of the focal point from the undercut site to a location where no undercut had occurred likely allowed holes to be generated at the surface of the wafer rather than at the subsurface etched feature. This would explain why the depth on the right-hand side of the etch slopes from the surface down to the depth where the entire structure should have been. A cross-sectional slice of the etch as measured by the optical profilometer. The deepest measured point is about 4 µm deep, which may not be accurate due to the high aspect ratio of the etched hole. However, this does clearly show the sloping increase in depth of the right hand side of the etch.

![Image of an attempt to etch and undercut expansion nozzle.](image)

**Figure C.6**: A profilometer image of an attempt to etch and undercut expansion nozzle.
Optical microscope images of an undercut membrane etch. This structure would be used for sonar resonator structures. The 3-axis stage used at this time made unpredictable movements, resulting in the entrance hole being severely off center. An optical microscope image of the membrane etch with the focal plane moved 13 µm into the surface reveals a subsurface structure, as can be seen by the lightly colored in-focus area. A FIB cross-section of this etch is shown in Figure C.8.

Figure C.7: (Left) An optical microscope image of the surface of an undercut membrane etch. (Right) An optical microscope image of the membrane etch with the focal plane moved 13 µm into the surface.
An SEM image of a FIB cross-section of the membrane etch shown in Figure C.7. The etched region is definable by its lighter coloring than the surrounding SiC bulk. This lighter coloring is redeposited SiC from the FIB milling procedure. This image shows an undercut region that varies in depth. This suggests that the 3-axis stage was making unpredictable movements in the axial direction, resulting in the etched structure seen here. Despite the poor control of the etch depth, this etch shows that undercut volumes may be created using the TPA PEC technique. This is an example of a feature that cannot be formed in single crystal SiC with any other single or combination of traditional SiC machining techniques.

Figure C.8: An SEM image of a FIB cross-section of the membrane etch shown in Figure C.7.
An optical microscope image of an etched triangle enclosing four attempts at through wafer vias. Obvious errors in stage movement may be seen in the bottom of the four holes and on the left side of Figure C.10. While these holes did not continue through the entire wafer, they did give significant insight into the characteristics of etched pores in SiC using TPA PEC. Figure C.10 covers these insights in more detail.

Figure C.9: An optical microscope image of an etched triangle enclosing four attempts at through wafer vias.
SEM images of entrance holes to some of the holes shown in Figure C.9. The entrance to one of the holes has a very shallow angle of entry, forming what appears to be a curved hole into the surface with a resulting undercut. Little surface etching appears around the entrance to the hole, showing that etch selectivity is very high. The majority of visible surface etching occurs directly above the undercut portion of the hole, indicating that some hole generation is present in the layer between the subsurface feature and the surface of the wafer. Another SEM image of the entrance to the top through wafer via attempt shows the internal sidewalls of the hole. They exhibit high levels of surface roughness. This indicates that longer dwell times or a change in HF concentration may be necessary for polishing of the sidewalls.

Figure C.10: (Left) An SEM image of an attempt at a through wafer via with obvious errors in stage movements. (Right) An SEM image of the entrance to the top through wafer via attempt.