Strain Evolution of Annealed Hydrogen-Implanted (0001) Sapphire

A thesis submitted in partial satisfaction
of the requirements for the degree Master of Science
in Materials Science and Engineering

by

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Exfoliation is a technique used to remove a thin, uniform layer of material from the bulk that involves the annealing of hydrogen ion-implanted materials in order to initiate defect nucleation and growth leading to guided crack propagation. This study presents an investigation into the annealing process required to initiate blistering (an essential precursor to exfoliation) in (0001) sapphire implanted at room temperature with hydrogen ions.

Triple axis x-ray diffraction was used to characterize the evolution of the implanted layer for single crystal (0001) sapphire substrates implanted at room temperature at 360 keV with either a $5 \times 10^{16}$ cm$^{-2}$ or $8 \times 10^{16}$ cm$^{-2}$ dose of hydrogen ions. A simulation of the ion distribution in TRIM estimated that the projected range and thickness of the implanted layer for both doses was approximately 2.2 µm.

Following implantation, the implanted sapphire was annealed using a two-step annealing procedure. The first step was performed at a lower temperature, ideally to nucleate and coarsen
defects. Temperatures investigated ranged from 550 – 650 °C. The second step was performed at a higher temperature (800 °C) to induce further defect coarsening and surface blistering. After all annealing steps, triple axis ω/2θ and ω scans were taken to observe any changes in the diffraction profile – namely, any reduction in the amplitude and shift in the location of the fringes associated with strain in the crystal – which would correlate with defect growth and nucleation. It was found that significant strain fringe reduction first occurred after annealing at 650 °C for 8 hours for both doses; however, it was not clear whether or not this strain reduction was due primarily to hydrogen diffusion or to recovery of other defects induced during the ion implantation. The ω/2θ curves were then fit using Bede RADS in order to quantify the strain within the crystal and confirm the reduction of the strained layer within the crystal. Finally, Nomarski optical images of the sample surfaces were taken after each step to observe any visual changes or blistering that might have occurred. These optical images showed that the strain reduction observed using XRD did not correlate to blistering, as no blisters were observed in any of the optical images.

Experimental results showed that at temperatures below 650 °C, no significant strain reduction occurs in hydrogen ion implanted (0001) sapphire. It has also been determined that for (0001) sapphire implanted at room temperature, it was not possible to produce surface blistering after a two-step annealing process at 650 °C and 800 °C, although significant strain reduction did occur, and ω scans showed peak broadening with subsequent annealing, indicating increasing mosaicity and potential defect nucleation. This was in contrast to previous findings that asserted that for sapphire annealed at 650 °C, surface blistering was observable.[7] As previous findings were based on sapphire implanted at elevated temperatures, this may imply that the sapphire substrate reaches a higher temperature than expected during such implantation processes, which may account for the capability for surface blistering at a lower temperature. Conversely, for
room temperature ion implantation, temperatures greater than 800 °C may be necessary to first nucleate hydrogen platelet defects and then produce surface blistering.
The thesis of Christine Megan Wong is approved.

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Chapter 1: Introduction

1.1 Introduction

Sapphire has been identified as one of the hardest naturally occurring materials on the planet. Additionally, it conducts heat at low temperatures, exhibits good light transmission properties, and is highly rigid. These properties and more have opened up use of sapphire for space and military applications, and most recently, to consumer electronics. For example, in November 2013, GT Advanced Technologies Inc. announced that it had signed a multi-year supply agreement with Apple Inc. to provide sapphire material, presumably for the screens of the impending iPhone 6. Approximately half a year later, it patented a sapphire cover plate for cellular devices. This cover plate, which would be less than 50 µm thick was designed to be adhered to a glass underplate, thereby mitigating the high cost of a bulk sapphire screen, but creating a screen with high scratch resistance and compressive strength. Exfoliation was proposed as the mechanism by which to achieve this thin, uniform plate.

The process of layer exfoliation (or, as deemed by its originator, the “smart-cut” process) has grown in popularity as the method of choice to obtain thin (tens of microns-scale) layers of various materials: the technology originated for silicon-on-insulator structures in the mid-1990’s, and previous work done by our group has also explored the feasibility of layer exfoliation processing on various III-V materials and other ceramics: for example, Hayashi et al. investigated the evolution of the surface morphology and subsequent necessary exfoliation parameters of hydrogen-exfoliated InP, along with the effects of crystallinity upon the exfoliation of GaN, while Miclaus et al. investigated exfoliation of Cd$_{0.96}$Zn$_{0.04}$Te substrates. With regard to sapphire in particular, the layer exfoliation of sapphire was first studied by Huang, Tong, and Gösele, who demonstrated the feasibility of layer transfer for hydrogen-
implanted sapphire in 1998\textsuperscript{[7]}. One key feature of Huang, Tong, and Gösele’s study was the fact that ion implantation needed to be performed at elevated temperatures, which the authors asserted was necessary for successful exfoliation or blistering of the material. However, previous work performed by our group has demonstrated that for blistering and exfoliation of III-V materials, elevated temperatures during ion implantation is non-ideal, as it may contribute to premature exfoliation during implantation, and in fact unnecessary if lower temperature ion implantation is followed by an intermediate annealing step prior to layer transfer. The applicability of this concept to the exfoliation of sapphire is therefore desirable, and one of the primary objectives of this research was to see if indeed an intermediate temperature annealing step combined with a higher ion implantation energy in comparison to Huang, Tong, and Gösele’s study would enable blistering in preparation for exfoliation.

In sum, the objective of this research is to provide a new methodology for achieving thin layers of sapphire through the method of layer exfoliation, potentially for further applications in consumer electronics.

1.2 Organization

The background and theory of layer exfoliation and the characterization methods used in this study are explored in Chapter 2. Chapter 3 provides an overview of the experimental methodology and equipment used. Chapter 4 details the experimental results obtained and an analysis of those results. Chapter 5 provides a summary and conclusion for this study, along with some notes about potential future research directions.
Chapter 2: Background and Theory

2.1 Layer Exfoliation

The process of layer exfoliation to obtain a thin layer (100 nm - µm range) from a thick substrate was first posited in 1995, when Bruel introduced the “Smart-Cut” process for silicon-on-insulator (SOI) structures as an alternative to existing methods [2-4]. Since then, the technique has been extensively researched for silicon, silicon carbide (SiC), and more recently, III-V materials.

As described by Bruel, the “smart-cut” process consists of four steps. Step one is the implantation of hydrogen ions into a wafer. The implantation process creates point defects such as vacancies and interstitials, which produce dangling bonds. The implanted H atoms will then either passivate the dangling bonds to form X-H complexes (X being the host material) or form molecular H₂. In the case of a number of these X-H complexes forming in close proximity to one another, planar defects known as “platelets” will be formed. These platelets are essential for successful exfoliation or blistering of the material, and can be formed in any monocristalline material provided the implantation occurs at a sufficiently high dose [1]. For the ion implantation step, a minimum hydrogen dose for layer exfoliation can be estimated using Equation 1 below:

\[ \varphi_m = \frac{\gamma}{\alpha kT} \]  

Where \( \gamma \) is the bonding energy, \( \alpha \) is a parameter related to the efficiency of implanted hydrogen atoms at splitting, \( k \) is Boltzmann’s constant, and \( T \) is absolute temperature. The peak implantation depth of the implantation, which is controlled by the implantation energy, determines the thickness of the exfoliated layer. Huang, Tong, and Gōsele, who studied the layer transfer of sapphire, also asserted that implantation must occur at an elevated temperature (≥ 650
°C for sapphire). Their reasoning was that at lower temperatures, large numbers of point defects generated by the implantation would be generated and unable to be recovered; in turn, these defects would impede hydrogen diffusion, which is essential for blistering. However, previous work done by our group asserted that elevated temperatures during exfoliation was not necessary, and indeed, could actually lead to unintentional premature layer exfoliation, since the wafer would also experience self-heating, and therefore, could achieve the critical temperature required for exfoliation. Therefore, Hayashi et al. proposed cooling the wafers to -20 °C during implantation in order to avoid any accidental exfoliation, which could also lead to a more predictable defect state.

Step two of the layer transfer process involves hydrophilic, room temperature bonding of wafer A to wafer B. The purpose of this second wafer is to act as a “stiffener” that promotes lateral crack propagation and opposes vertical lift off. This is a necessary step in order to accomplish complete layer transfer, as for an unconstrained surface, defect growth will not continue in a purely lateral direction, leading to the exfoliation of small (micron scale) fragments. The stiffener is added after the implantation step in order to prevent plastic deformation during implantation.

Step three is a heat treatment step. The original formulation of the smart-cut process involves a two-step heat treatment. The first step initiates the exfoliation by causing the nucleated defects to coarsen and grow, such that layer splitting is achieved. This occurs as a result of X-H complex dissociation, which frees up H atoms that then diffuse into the platelets to form molecular H₂ gas. This leads to the creation of microcracks, and subsequent H diffusion increases the internal pressure inside these cracks, causing the cracks to grow, leading to layer splitting. The second step serves to strengthen the chemical bonds between the two wafers.
Previous work done by our group reversed the order of these steps, proposing a lower temperature anneal (the exact “lower temperature” is material-dependent) to strengthen the bonds between the two wafers and encourage defect coarsening, followed by annealing at an elevated temperature to exfoliate. Hayashi et al. posited that the effects of this lower temperature anneal were similar to those that occur as a result of ion implantation at elevated temperatures. Additionally, at this lower temperature, there is no risk of accidental exfoliation, since the activation energy for splitting is much higher and dependent on mechanisms other than hydrogen diffusion. [9]

The final step in the smart-cut process is a final polish of the exfoliated layer surface to achieve a desired surface roughness if necessary. For sapphire, this may be done using chemical mechanical polishing (CMP).

2.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a characterization technique that relies upon the phenomenon of diffraction to provide information about crystals such as the crystal orientation and lattice parameter. In most diffractometers, a mounted sample is positioned at an angle corresponding to the Bragg angle for a specified allowed reflection relative to an x-ray source and a detector. Prior to impingement upon the sample, the x-ray beam is collimated such that the incident x-rays are mostly monochromatic. Following impingement upon the sample, the diffracted beams may be passed through a second collimating system prior to being received by the detector; in this case, the diffractometer is considered to be in “triple-axis” mode, while the case without this second collimating system is considered “double-axis” mode.
As mentioned previously, x-ray diffraction can be used to determine the lattice parameter of a crystal. This ability can be extended further to examine variations in the lattice parameter in the instance of imperfect and strained crystals. In 1987, Servidori proposed multiple axis XRD as an alternative to transmission electron microscopy (TEM) and other established methods of structural analysis for the examination of crystal damage generated by ion implantation. This was based off the observation that for ion implanted materials, since the thickness of the surface layer containing implantation-induced defects was less than the extinction length of x-rays, the rocking curves (ω scans) of these materials differed significantly from those for perfect crystals, as the defects introduced asymmetry, additional satellite peaks, and tail oscillations into the curves. Servidori found that the strain distribution could be determined by modeling the experimental curve with a simulated curve that assumed the crystal to be composed of multiple layers of varying strain, such that the strain versus depth relationship could be plotted. This distribution in turn could be correlated to implantation profile parameters such as the straggle and range. Additionally, the maximum strain has been found to be proportional to the implantation dose. Moulet & Goorsky also found that the diffraction profile (ω-2θ scan) for implanted crystals evolved based on the annealing temperature: in particular, they noted a reduction of the fringes in the profile associated with the strain distribution after annealing, which corresponded to a reduction in the strain. Because of this phenomenon, the evolution of the diffraction profile provides a way of tracking the evolution of defects within the crystal and determining when the defects have sufficiently coarsened such that smooth crack propagation across the layer is feasible. Triple axis rocking curves can also be used to assess the mosaicity change in the sample as a result of annealing, which results from the presence of platelets inside the crystal that bend the lattice.
2.3 Nomarski Microscopy

Nomarski microscopy, or differential interference contrast (DIC) microscopy, is a type of optical microscopy that is useful to image transparent samples with features that may be difficult to observe using traditional optical microscopy methods through enhanced image contrast. The setup for Nomarski microscopy is similar to traditional optical microscopy, with the additional of a Wollaston prism to the back focal plane of the objective lens and a slit diaphragm to the front focal plane of the condenser lens. When a planar, polarized light wave passes through the sample, the light wave undergoes a local phase shift that corresponds to the optical path difference occurring in the object. It then passes through the objective lens and the Wollaston prism in the back focal plane, which shears the wave into two wave fronts that are polarized at right angles. When these two wave fronts then pass through the analyzer, they interfere, creating an image of an otherwise transparent feature.

2.4 Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM)

Focused ion beam-scanning electron microscopy (FIB-SEM) is a dual-beam system composed of an electron column and an ion column. In scanning electron microscopy (SEM), a focused electron beam is scanned across a sample face. The interactions between the beam and the sample surface result in the generation of different signals which may be detected and used to generate an image of the sample surface. Focused ion beam (FIB) is a technique similar to SEM, except that a beam composed of ions (typically gallium) as opposed to electrons is focused and scanned across the surface. When operated using a high beam current, FIB can be used to mill samples. For cross section preparation, typically, a layer of conductive material such as platinum
(Pt) is deposited over the area of interest; this layer both protects and smooths the surface. The FIB is then directed to mill into the area covered by the Pt layer.

When the two techniques are combined in a single system, as in FIB-SEM, they are particularly useful for obtaining cross sectional images of materials, as the electron beam can be used to monitor the cross-section face of the sample as the ion beam mills normal to the surface. In most configurations, the ion column is tilted 52° relative to the vertical, requiring the sample to be likewise tilted in order to achieve milling in the normal direction. Images may be obtained either after or during milling. Typically, the electron beam is used for imaging, as SEM yields higher resolution images than FIB, although the ion beam may be used too, as it offers excellent image contrast. \[16\]
Chapter 3: Experimental Methods

3.1 Hydrogen Ion Implantation

Hydrogen ion implantation was performed on 2-inch diameter (0001) sapphire wafers using facilities at Cutting Edge Ions in San Diego. The sapphire wafers were obtained from Precision Micro-Optics. The implantation was performed at room temperature (approximately 25 °C) at an implantation energy of 360 eV. One wafer was implanted with a dose of $5 \times 10^{16}$ cm$^{-2}$ H ions; another with a dose of $8 \times 10^{16}$ cm$^{-2}$ H ions.

3.2 Damage Characterization via Triple Axis X-ray Diffraction

To characterize the strain profile in the implanted samples, $\omega/2\theta$ diffraction scans were taken about the (006) reflection using triple axis diffraction (TAD). The range of these scans was approximately -1500 to 500 arcsec. Additionally, $\omega$-curves, or rocking curves, were also taken about the (006) reflection to examine the mosaicity of the main peak. The range of these scans was approximately -150 to 150 arcsec. To perform TAD, a Bede D1 diffractometer using copper Ka radiation and two-bounce (220) Si. The step size used was 3 arcsec. Scans were not conducted using a universal count time – that is, the count time of one scan would not necessarily match the count time of a later scan. The selected count time fell typically in the range of 15 – 60 seconds. The generated diffraction profiles were then simulated using Bede RADS, an analytical software designed for modeling diffraction profiles.

3.3 Annealing of Implanted Sample

To investigate the effects of annealing at different elevated temperatures, two sapphire wafers – one implanted with a dose of $5 \times 10^{16}$ cm$^{-2}$ H ions and one implanted with a dose of
8x10^{16} \text{ cm}^{-2} \text{ H ions} – were cleaved into approximately 1x1 \text{ cm}^2 pieces. Figure 1 below shows an example of the results of this process.

![Image of cleaved sapphire]

**Figure 1: Example of 5x10^{16} \text{ cm}^{-2} \text{ H ion-implanted sapphire cleaved into 1x1 \text{ cm}^2 pieces}**

Each piece was then annealed at the desired elevated temperature in a box furnace. Investigated temperatures for the first annealing step were 550 °C, 600 °C, and 650 °C. Prior to annealing, each sample was characterized using TAD in order to account for the possibility of variation in the implantation strain. Samples were first annealed for 1 hour, then characterized using TAD. After characterization, samples were then annealed again at the same temperature for 7 hours (8 hours total), characterized, and then finally annealed for an additional 16 hours (24 hours total) and characterized via TAD.
3.4 Sample Imaging

Following each annealing step, the implanted samples were also inspected for signs of blistering using Nomarski microscopy. Prior to imaging, the samples were cleaned using a 1:1:5 mixture of H₂O₂:NH₂OH:H₂O followed by a solvent rinse, in order to remove any organic contamination or particles on the sample following annealing and XRD. The microscope used was a Nikon Eclipse ME600, and all images were taken using a lens magnification of 5x. Images were recorded digitally using the Q-Capture software.

To investigate the presence of a sub-surface damaged layer, FIB-SEM imaging was done using a FEI NOVA 600 FIB. A thin layer of gold was first sputtered onto a sample in order to create a conductive surface. A FIB cut was then made to a depth of approximately 3 µm in order to ensure capture of the damaged layer, assuming a projected range of approximately 2.2 µm.
Chapter 4: Data and Discussion

4.1 Characterization of As-Implanted Sapphire

4.1.1 Determination of Implantation Projected Range

Selection of the ion implantation parameters is dependent upon the desired layer thickness. Typically, exfoliation occurs at a depth corresponding to a maximum in the implanted ion distribution, or the implantation projected range. Estimating the projected range can be done using SRIM, a program designed to determine ion implantation distribution characteristics. Figure 2 shows the projected range for a 360 kV hydrogen ion implantation into sapphire, as determined by SRIM.

Figure 2: TRIM-generated simulation of a 360 kV hydrogen ion implantation into Al₂O₃ and distribution parameters.

However, SRIM has limitations: it does not take into account other implantation parameters such as implantation temperature and dose. These parameters can cause the projected
range to deviate from SRIM’s estimate. Therefore, it is unreliable to depend upon the projected range produced by SRIM, and an accurate, non-destructive method of determining the projected range within an implanted crystal is desired. This method has been previously described at length by members of our group, and involves the use of x-ray diffraction (XRD) to track the diffusion/movement of ions within the crystal.

Previous research on ion implantation has shown that the measured strain in the crystal as a result of ion implantation is proportional to the energy lost in nuclear collisions ($F_D$), or recoil energy. $^{[17]}$ In particular, the maximum strain within the crystal occurs where the recoil energy is a maximum, such that

$$
\varepsilon_{\perp,\text{max}} = K \cdot \Phi \cdot F_{D,\text{max}} \tag{2}
$$

where $\Phi$ is the implant dose (ions/Å$^2$) and $K$ is a constant. $^{[14, 15]}$

As a brief aside, although some research indicated that this relationship only held for low doses of heavy ions, and that $K$ changed depending on the material, it has since been shown that for low temperature implantation, $K$ holds constant for a given species in different materials, since the low temperature implantation impedes the mechanisms responsible for changes in $K$, namely defect motion, trapping, or defect recombination. $^{[15]}$ Therefore, this relationship also applies to crystals implanted with high doses of light ions, such as hydrogen.

In any case, the relationship described by (2) is relevant because the distribution of recoil energy in turn is proportional to the distribution of hydrogen ions within the crystal. Therefore, knowing the strain distribution within the crystal is equivalent to knowing the ion distribution within the crystal. This enables use of the strain profile to track the diffusion of hydrogen ions within the crystal and nucleation of hydrogen platelet defects.
4.1.2 X-Ray Diffraction

Triple axis x-ray diffraction measurements were taken of the as-implanted samples in order to characterize the strain generated by the implantation process and establish a baseline for comparison after annealing. Using the program Bede RADS, the generated \(\omega/2\theta\) curves were then fit in order to generate the strain profile. The shape of the strain profile was assumed to be Gaussian, with the peak located at the projected range estimated by SRIM.

4.2 XRD Characterization of Strain Evolution for Annealed Sapphire

In order to induce surface blistering without the use of ion implantation at elevated temperatures, a two-step annealing procedure is required. The first annealing step is done to compensate for the lower implantation temperature: it provides the energy required for defect nucleation and hydrogen diffusion to platelet defects, and also heals implantation damage. The procession of these processes may be tracked via the evolution of the diffraction profile of the sample. For strained crystals, the diffraction profile will contain distinct fringes; the periodicity of these fringes provides information about the width of the strained layer in the crystal, while the location of the most distant fringe from the main or substrate peak corresponds to the maximum strain within the crystal. Therefore, any changes in the diffraction fringes corresponds to changes in the strain profile. For the first annealing step, if sufficient defect nucleation and hydrogen diffusion have occurred, it is expected that the diffraction fringes will significantly decrease, indicating that the strain in the crystal has been released via the formation of defects, and potentially due to recovery of damage from the implantation. Table 1 below shows the annealing times and temperatures investigated for the first annealing step, along with the doses of the samples used.
<table>
<thead>
<tr>
<th>Annealing Temperature / Time (Total)</th>
<th>5x10(^{16}) cm(^{-2}) dose</th>
<th>8x10(^{16}) cm(^{-2}) dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>550 °C</td>
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<tr>
<td>1 hr</td>
<td>X</td>
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<td>8 hr</td>
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<tr>
<td>24 hr</td>
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<tr>
<td>24 hr</td>
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</tr>
</tbody>
</table>

Table 1: Chart of first step annealing times/temperatures investigated

550 °C was selected initially for investigation based on findings from Huang, Tong, and Gösele, who indicated that after implanting at 650 °C, they were able to achieve blistering on the surface of sapphire. As no blistering is supposed to occur during the first annealing step, it was necessary to choose a temperature that would potentially provide the necessary thermal budget for ion diffusion, but that also lay below the confirmed blistering temperature of 650 °C.

4.2.1 5x10\(^{16}\) cm\(^{-2}\) Dose H-Implanted Sapphire

Figure 3 below shows the evolution of the diffraction profile for a 5x10\(^{16}\) cm\(^{-2}\) dose sapphire sample annealed consecutively at 550 °C for 1 hr, 8hr, and then 24 hr.
Figure 3: Evolution of $\omega/2\theta$ scan of the (006) reflection for sapphire implanted with a $5 \times 10^{16}$ cm$^{-2}$ dose of hydrogen ions after annealing at 550 °C.

Figure 4: Modeled evolution of strain inside $5 \times 10^{16}$ cm$^{-2}$ H-implanted sapphire after annealing at 550 °C for up to 24 hrs.
As seen above, at 550 °C, while a change in the strain profile occurs after annealing for one hour, no subsequent change occurs after further annealing. Additionally, the change that does occur is not affiliated with a decrease in strain, as the location of the most distant strain fringe, which provides a rough benchmark for the maximum strain in the crystal, does not move closer to the main peak after any extended period of annealing. RADS analysis of the XRD data (Figure 4) confirms that after 1 hr of annealing, the strain within the crystal is relatively consistent after up to 24 hours of annealing, which implies that the strain produced by the hydrogen implantation did not change measurably occurred beyond 1 hour of annealing. This suggests that at 550 °C, there is insufficient energy for hydrogen diffusion to occur, which would lead to further strain relaxation. The profile changes seen after 1 hour of annealing are probably due to the recovery of damage generated during the implantation process, which would be the other source of strain within the crystal. From this, it can be concluded that 550 °C is not a suitable temperature for the first annealing step. This led to the selection of 650 °C as the second temperature to investigate. Although this would seem to conflict with the desire to avoid premature blistering in correspondence with Huang, Tong, and Gösele, investigation at 650 °C was necessary because any temperature lower than 550 °C would not lead to hydrogen diffusion, the primary aim of the first annealing step.

Figure 5 shows the evolution of the ω/2θ curve after annealing at 650 °C for one hour and then eight hours total for sapphire samples implanted with 5x10^{16} and 8x10^{16} cm^{-2} doses of hydrogen ions. Annealing at 650 °C for eight hours appeared to have had a significant effect upon the diffraction profile – namely, a decrease in fringe contrast and broadening. This is consistent with strain reduction as a result of hydrogen diffusion and the healing of point defects generated during implantation. RADS analysis of the diffraction profile confirmed annealing for
8 hrs had halved the strain in the crystal (Figure 12). Further examination of the growth of hydrogen platelets within the crystal was done through TAD $\omega$ scans, which are shown below in Figure 6.

![Graph showing evolution of $\omega/2\theta$ scan of the (006) reflection for sapphire implanted with a $5 \times 10^{-16}$ cm$^{-2}$ dose of hydrogen ions after annealing at 650 °C.]

**Figure 5:** Evolution of $\omega/2\theta$ scan of the (006) reflection for sapphire implanted with a $5 \times 10^{-16}$ cm$^{-2}$ dose of hydrogen ions after annealing at 650 °C.
Figure 6: Evolution of $\omega/2\theta$ scan of the (006) reflection for sapphire implanted with a) $5 \times 10^{-16}$ cm$^{-2}$ dose of hydrogen ions and b) $8 \times 10^{-16}$ cm$^{-2}$ dose of hydrogen ions after annealing at 650 °C

For sapphire implanted with a $5 \times 10^{16}$ cm$^{-2}$ dose of hydrogen ions, after annealing at 650 °C for 8 hours, the full width at half maximum (FWHM) increased, indicating mosaic tilt within the crystal affiliated with the growth of hydrogen platelets within the crystal, which is desired for blistering and exfoliation.

Because of the resulting decrease in the strain fringes and increase in the FWHM, an assumption was made that annealing at 650 °C for eight hours was sufficient to nucleate and grow the hydrogen platelets needed for blistering. Therefore, a second annealing process was conducted to further grow the platelets to a diameter large enough that microcracks would be able to form and blistering could occur. The temperature investigated for this step was 800 °C.

Following annealing at 650 °C for eight hours, a sapphire sample was then annealed at 800 °C.
for five hours and characterized via TAD $\omega/2\theta$ and $\omega$ scans. Figure 7 shows the effects of this higher temperature anneal.

![Graph showing effects of higher temperature anneal](image)

**Figure 7: Evolution of $\omega/2\theta$ and $\omega$ curves for the (006) reflection of sapphire implanted with a $5\times10^{16}$ cm$^{-2}$ dose of hydrogen ions following annealing at 650 °C for 8 hrs and 800 °C for 5 hrs**

Examining the $\omega/2\theta$ curve following the 800 °C anneal, it is clear that further strain reduction occurred; additionally, the $\omega$ curve shows further increase in the FWHM, which would
indicate further hydrogen platelet growth and suggest the potential presence of blistering. To confirm whether or not the sample surface had blistered, Nomarski optical images were taken. (Figure 8) However, these images showed no evidence of blistering on the surface after annealing. This suggested that although the strain had been further reduced and the platelets further grown, potentially, more annealing, either at a higher temperature or for a longer time, was needed in order for blistering to actually occur.

Figure 8: Nomarski images of a 5x10^{16} cm^{-2} hydrogen-implanted sapphire sample a) before annealing and b) after annealing for 8 hrs at 650 °C and for 5 hrs at 800 °C
There was also the possibility that as a result of repeated thermal cycling, the hydrogen had diffused entirely out of the crystal. This would explain why strain reduction was seen, but no blisters were observed. To examine this possibility, samples were cross-sectioned using FIB-SEM in order to verify the continued existence of an implanted layer. (Figure 9)

![FIB-SEM image of 5x10^16 cm^-2 H-ion implanted sapphire annealed for 24 hrs at 650 °C and 5 hrs at 800 °C](image)

Figure 9: FIB-SEM image of 5x10^16 cm^-2 H-ion implanted sapphire annealed for 24 hrs at 650 °C and 5 hrs at 800 °C

The FIB-SEM images showed that a damaged layer still existed within the crystal, indicating that the non-presence of blisters was not a result of complete diffusion of hydrogen out of the crystal into the environment. With this confidence, the samples were annealed an additional three hours at 800 °C to see if blistering could be produced. However, it appeared that
there was no change in the diffraction profile after this extended anneal. (Figure 10) RADS analysis confirmed that no additional strain reduction had occurred, meaning that no further hydrogen diffusion occurred, and thus, no platelet growth had occurred. (Figure 12) Nomarski images also confirmed that no blistering was accomplished by the lengthened anneal. (Figure 11) The lack of change in the strain profile after annealing begs the question of what might be impeding further diffusion. Potentially, it could be that some point defects introduced during ion implantation have not been recovered and therefore could be impeding ion diffusion. It could also be that throughout the second, higher temperature anneal, hydrogen is diffusing both out of the crystal and toward the maximum range. This would result in only a fraction of the originally-implanted hydrogen reaching the maximum range, which could impede defect nucleation. In this case, a larger ion dose might be required.
Figure 10: Evolution of $\omega/2\theta$ and $\omega$ curves for the (006) reflection of sapphire implanted with a $5 \times 10^{16}$ cm$^{-2}$ dose of hydrogen ions following annealing at 650 °C for 8 hrs and 800 °C for 5 hrs.
Figure 11: Nomarski images of a $5 \times 10^{16} \text{ cm}^{-2}$ hydrogen-implanted sapphire sample a) after annealing for 8 hrs at 650 °C and 5 hrs at 800 °C and b) after annealing 8 hrs at 650 °C and 5 hrs at 800 °C

Figure 12: Modeled evolution of strain inside $5 \times 10^{16} \text{ cm}^{-2}$ H-implanted sapphire after annealing at 650 °C and 800 °C

Since additional annealing at the second annealing temperature was insufficient to produce blistering, the possibility of needing to lengthen the first annealing step was explored.
This possibility was considered to address the concern that even though annealing at 650 °C for eight hours was sufficient to nucleate the hydrogen defects, they needed more time to coarsen such that at the higher temperature, they would be able to form microcracks. This was done by increasing the annealing time at 650 °C to 24 hours total before annealing at 800 °C for five hours. Annealing at 800 °C was not extended to eight hours, since previous samples’ results had shown that annealing at 800 °C for eight hours as opposed to five hours did not lead to any change in the strain profile. The results of this process are shown in Figure 13.

Similar to samples annealed at 650 °C for eight hours prior to the second annealing step, annealing initially at 650 °C for 24 hours led to significant fringe reduction relative to the as-implanted state. However, after the second annealing step at 800 °C, there was no visual indication of blistering, as shown in Figure 14.
Figure 13: Evolution of \( \omega/2\theta \) and \( \omega \) curves for the (006) reflection of sapphire implanted with a \( 5 \times 10^{16} \text{ cm}^{-2} \) dose of hydrogen ions following annealing at 650 °C for 24 hrs and 800 °C for 5 hrs.
Comparing the TAD XRD curves for the extended annealing time at 650 °C to those for the previous time of eight hours also showed that the two curves matched (Figure 15), suggesting that extending the annealing time at 650 °C to 24 hours did not have any effect upon the hydrogen platelets’ ability to coarsen/grow during the elevated temperature anneal. Similarly, modeling the TAD curves in RADS showed that the strain profile of the sapphire piece annealed initially at 650 °C for 24 hr after the second anneal at 800 °C mirrored the final strain profile of the sapphire piece annealed initially at 650 °C for 8 hr, which verified that extending the length of the initial lower temperature anneal did not have an effect upon hydrogen diffusion. (Figure 16) Therefore, it was concluded that the proposed two-step annealing process at 650 °C and 800 °C could not produce blistering on the surface of sapphire implanted with a dose of $5 \times 10^{16}$ cm$^{-2}$ hydrogen ions.
Figure 15: Comparison of $\omega/2\theta$ and $\omega$ curves at the (006) reflection for $5 \times 10^{16}$ cm$^{-2}$ H-implanted sapphire annealed at 650 °C for 24 hours and 800 °C for 5 hours, and annealed at 650 °C for 8 hours and 800 °C for 8 hours.
Figure 16: Modeled evolution of strain inside $5 \times 10^{16} \text{cm}^{-2}$ H-implanted sapphire after annealing at 650 °C and 800 °C. Annealing at 650 °C was extended in some cases to 24 hours.

4.2.2 $8 \times 10^{16} \text{cm}^{-2}$ Dose H-Implanted Sapphire

A two-step annealing process at 650 °C and 800 °C was also applied to sapphire samples implanted with a dose of $8 \times 10^{16} \text{cm}^{-2}$ of hydrogen ions to see if a higher dose affected the conditions required for surface blistering. A sample was first annealed at 650 °C for 8 hours and then at 800 °C for 5 hours, following the procedure tested for samples implanted with the $5 \times 10^{16} \text{cm}^{-2}$. Figure 17 shows the ω/2θ and ω curves for this annealing procedure.

Similar to the sample implanted with a dose of $5 \times 10^{16} \text{cm}^{-2}$ hydrogen ions, annealing at 650 °C for 8 hours led to a decrease in the strain fringes. However, in comparison to the samples implanted with a $5 \times 10^{16} \text{cm}^{-2}$ dose, the difference in FWHM from the as-implanted sample and after annealing for 8 hours at 650 °C was not as profound. This suggests that the decrease in the fringes – corresponding to an approximate 40% decrease in strain (Figure 18) – seen after
annealing was due mainly to other damage recovery mechanisms, with the contribution from hydrogen diffusion as secondary.

After annealing at 800 °C for 5 hours, peak broadening was observed in the ω scan, suggesting that hydrogen diffusion had occurred, and therefore, hydrogen platelets had grown in the crystal. However, visual examination of the sample using Nomarski microscopy did not indicate any sign of blistering. (Figure 19) Lengthening the 800 °C anneal to 8 hours was also explored; however, the results were similar to those for sapphire implanted with a $5 \times 10^{16}$ cm$^{-2}$ dose, in that the diffraction profile remained unchanged, indicating that no additional strain reduction had occurred.
Figure 17: Evolution of $\omega/2\theta$ and $\omega$ curves for the (006) reflection of sapphire implanted with an $8 \times 10^{16}$ cm$^{-2}$ dose of hydrogen ions following annealing at 650 °C for up to 8 hrs and 800 °C for up to 8 hrs.
Figure 18: Modeled strain evolution for a sapphire sample implanted with an $8 \times 10^{16}$ cm$^{-2}$ dose of hydrogen ions, annealed at 650 °C and 800 °C.

Figure 19: Nomarski images of a $8 \times 10^{16}$ cm$^{-2}$ hydrogen-implanted sapphire sample a) after annealing for 24 hrs at 650 °C and b) after annealing 24 hrs at 650 °C and 5 hrs at 800 °C

Additionally, the effects of extending the first annealing step at 650 °C from 8 hr to 24 hr were explored. The resulting $\omega/2\theta$ and $\omega$ scans (Figure 20) and strain analysis (Figure 22) showed that annealing for 24 hr at 650 °C was effective at reducing the strain within the crystal.
reducing it by about 80%. Additionally, the FWHM of the $\omega$ increased after the 24 hour anneal. This clarifies the findings for the 8 hour anneal, in which strain reduction was noticed, but there was not significant increase in the FWHM. It appears that up to around 8 hours, the predominant mechanism of strain recovery is unrelated to hydrogen diffusion; longer annealing times are needed for the ions to begin diffusing to the projected range. However, even with the extended 650 °C anneal, there was no observed surface blistering following the 800 °C anneal, similar to the results for the $5 \times 10^{16}$ cm$^{-2}$ dose implanted sapphire. (Figure 21). Using RADS, it was shown that the end state of the strain distribution within the crystal was identical to that of previous samples annealed for a shorter amount of time at 650 °C. This would seem to indicate a limitation with selecting 800 °C as the higher temperature for the second annealing step: at this temperature, there is insufficient energy to grow the nucleated hydrogen platelets such that microcracks can form. This would imply that a higher temperature (for example, 1000 °C) may be necessary to initiate blistering.
Figure 20: Evolution of $\omega_{/2\theta}$ and $\omega$ curves for the (006) reflection of sapphire implanted with an $8 \times 10^{16}$ cm$^{-2}$ dose of hydrogen ions following annealing at 650 °C for 24 hrs and 800 °C for 5 hrs.
Figure 21: Nomarski images of an $8 \times 10^{16}$ cm$^{-2}$ hydrogen-implanted sapphire sample a) as-implanted and b) after annealing for 24 hrs at 650 °C and 5 hrs at 800 °C.

Figure 22: Evolution of modeled strain profile of $8 \times 10^{16}$ cm$^{-2}$ H-implanted sapphire. Annealing at 650 °C was extended to 24 hrs from 8 hrs.
Chapter 5: Conclusion and Future Work

Using ion implantation, C-plane sapphire samples were implanted with hydrogen ions in doses of $5 \times 10^{16}$ cm$^{-2}$ and $8 \times 10^{16}$ cm$^{-2}$ at room temperature and an accelerating voltage of 360 kV. The effects of annealing with intent to produce surface blisters was then investigated. Samples were first annealed at 550 °C and 650 °C to encourage hydrogen ion diffusion and defect nucleation as a precursor to blistering. Triple axis x-ray diffraction was used to track the evolution of the crystal strain as a result of annealing. ω/2θ curves taken about the (006) reflection were fit using the RADS software in order to determine the strain distribution in the crystal following annealing. ω curves were also taken in order to observe changes in mosaicity, which would indicate the nucleation and coarsening of hydrogen platelet defects. It was determined that at 550 °C, there was insufficient thermal budget for hydrogen diffusion: after up to 24 hours of annealing, RADS analysis showed that no strain reduction had occurred, and all changes in the diffraction profile were due to redistribution of strain within the crystal. For samples annealed at 650 °C, hydrogen diffusion was assumed following 8 hours of annealing for samples implanted with $5 \times 10^{16}$ cm$^{-2}$ H$^+$, and 24 hours of annealing for samples implanted with $8 \times 10^{16}$ cm$^{-2}$ H$^+$, based on observations from the resulting ω curves: for samples implanted with $5 \times 10^{16}$ cm$^{-2}$ H$^+$, following 8 hours, strain reduction was observed in addition to an increase in the FWHM. For samples implanted with $8 \times 10^{16}$ cm$^{-2}$ H$^+$, an increase in the FWHM was not noticed until after 24 hours of annealing.

Under the assumption that an initial annealing step of 650 °C had led to sufficient defect nucleation and strain reduction, samples were annealed at 800 °C for up to 8 hours to initiate blistering. RADS analysis of the resulting ω/2θ curves showed that additional strain reduction had occurred, implying that defects had coarsened and blisters may have formed. Using
Nomarski microscopy, however, it was shown that no blisters occurred in all samples. These findings establish that a two-step annealing process for similarly-implanted sapphire at 650 °C and 800 °C is insufficient to produce surface blistering – and, for bonded samples, layer exfoliation.

Future work on this topic first must naturally address the determination of the exact temperature ranges necessary for surface blistering or layer exfoliation of sapphire implanted at room temperature. One potential direction may be sprung from the observation that strain reduction stopped after a set time when annealing at 800 °C, regardless of the length of time for which the sample was annealed at the lower temperature of 650 °C, and no blistering was ever observed. One potential explanation for this observation could be that 800 °C may lie in the temperature range in which hydrogen diffusion is the primary mechanism of strain reduction, as opposed to defect growth: strain reduction would cease if all the available hydrogen ions had already diffused to the maximum range, and defects had been nucleated. However, more energy is required for those nucleated defects to then grow to sufficient size so as to produce blisters or microcracks. Therefore, an alternative process that should be explored would involve first annealing the sample at 800 °C for 5 hours, and then annealing at a higher temperature such as 1000 °C to see if blistering could be observed.
References


